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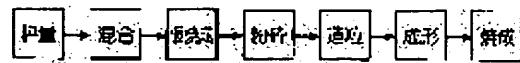
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(54) DIELECTRIC CERAMIC FIRED AT LOW TEMPERATURE, MULTILAYER TYPE DIELECTRIC ELEMENT, METHOD OF PRODUCING THE DIELECTRIC CERAMIC AND AUXILIARY OXIDE

(57)Abstract:

PROBLEM TO BE SOLVED: To fire a PZT-based dielectric ceramic at a desired low temperature and to prevent lowering of the performance of a base material.

SOLUTION: The dielectric ceramic is obtained by providing a mixture or a calcined material of raw materials for the dielectric ceramic containing, as a main component, a composition having a dielectric ceramic composition of ABO₃-type, wherein, when B site is defined as 1, A site is Pb contained in a molar ratio of ≥ 0.9 , then adding, as auxiliary oxides, PbO_x+(WO₃_y+MoO₃_z) (wherein, x+y+z=1; 0.005< y+z<0.4; and y, z ≥ 0) in an total amount of 0.05 to 20 mol.% to the mixture or the calcined material above, mixing, forming and firing the formed body. The total amount of tungsten and molybdenum in the fired body is lower than 0.098 moles when the molar amount of Pb is set to be 1, and the density of the fired body is ≥ 7.5 g/cm³. The auxiliary oxides are dispersed in the calcined powder, form a liquid phase at a desired temperature and accelerate firing, thereby it becomes possible to fire at a low temperature.



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CLAIMS

[Claim(s)]

[Claim 1] ABO_3 When it has the dielectric ceramic presentation of a mold and B site is set to 1, while using as a principal component the constituent which contains the lead of 0.9 or more mole ratios to A site At least one sort in a tungsten and molybdenum is contained, and the consistency after baking is 3 7.5g/cm. Low-temperature baking-ized dielectric ceramics which is above and is characterized by being smaller than 0.37 mole ratios when the content of the sum total of a tungsten and molybdenum sets lead to 1.

[Claim 2] Low-temperature baking-ized dielectric ceramics according to claim 1 with which a tungsten and molybdenum are arranged in the grain boundary at high concentration rather than the inside of the grain of the dielectric ceramics.

[Claim 3] either of above-mentioned claims 1 or 2 -- the laminating mold dielectric element which has the laminated structure which made the electrode layer to which the melting point which uses copper as a principal component uses an electrode layer or silver thru/or silver, and palladium 1083 degrees C or less as a principal component intervene between the layers of the low-temperature baking-ized dielectric ceramics of a publication.

[Claim 4] Above-mentioned claims 1 or 2 are the approaches of manufacturing the low-temperature baking-ized dielectric ceramics of a publication, either, the assistant oxide which blended at least one sort of oxide with the plumbic acid ghost at the following rate of a compounding ratio among a tungsten and molybdenum is used, and it is $PbO_x + (WO_3 y + MoO_3 z)$.

However, $x+y+z=1$, $0.005 < y+z < 0.4$, y , and $z >= 0$ ABO_3 It has the dielectric ceramic presentation of a mold. When B site is set to 1, the constituent which contains the lead of 0.9 or more mole ratios to A site in the raw material mixture or the temporary-quenching object of the dielectric ceramics used as a principal component The manufacture approach of the dielectric ceramics which carries out addition combination of the above-mentioned assistant oxide at 0.05-mol % - 20-mol % of a rate, and is characterized by mixing, fabricating and calcinating.

[Claim 5] The manufacture approach of the dielectric ceramics according to claim 4 of obtaining at least one sort of oxide for the above-mentioned assistant oxide among a tungsten and molybdenum to a plumbic acid ghost dry type or by carrying out wet blending, or carrying out wet blending, and grinding dry type or after carrying out temporary baking.

[Claim 6] The manufacture approach of the dielectric ceramics according to claim 4 or 5 which makes the amount of the lead raw material in the above-mentioned raw material mixture the amount which reduced a supplied part from the lead oxide of the above-mentioned assistant oxide in the process which prepares the raw material mixture of the above-mentioned dielectric ceramics.

[Claim 7] 6 is [claim 4 using the above-mentioned assistant oxide which has the melting point from the temperature used as 3% of self-contraction of the above-mentioned dielectric ceramics before the completion temperature of contraction thru/or] the manufacture approach of the dielectric ceramics a publication either.

[Claim 8] The sheet which added the above-mentioned assistant oxide is used for the temporary baking powder which carried out temporary quenching of raw material powder or the raw material powder when fabricating the above-mentioned dielectric ceramics in the shape of a sheet, and 7 is [printing, claim 5 which carries out a laminating and carries out coincidence baking, or] the manufacture approach of the dielectric ceramics a publication either about an electrode layer to this.

[Claim 9] Assistant oxide which is the assistant oxide used as an assistant at the time of sintering the ceramics, comes to blend at least one sort of oxide with a plumbic acid ghost among a tungsten and molybdenum, and is characterized by the sum total content of a tungsten and molybdenum being more greatly [than 0.5 mol %] smaller than 40-mol %.

[Claim 10] Assistant oxide which is the assistant oxide used as an assistant at the time of sintering the ceramics, comes to carry out temporary quenching of the mixture which blended at least one sort of oxide with the plumbic acid ghost

among a tungsten and molybdenum, and is characterized by the sum total content of a tungsten and molybdenum being more greatly [than 0.5 mol %] smaller than 40-mol %.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the assistant oxide for making possible the dielectric ceramics included while composing lead especially the dielectric ceramics in which low temperature sintering is possible, its manufacture approach, and low temperature sintering.

[0002]

[Description of the Prior Art] Although the dielectric ceramics of a PZT (titanic-acid lead zirconate) system is useful as ingredients, such as a piezoelectric transformer and an electrostrictive actuator, there is fault that burning temperature needs to use refractory metals with a possibility that lead oxide (PbO) may evaporate that it is an elevated temperature, and a desired sintered compact presentation may not be acquired, such as platinum (Pt) expensive as an internal electrode ingredient, and serves as cost quantity. For this reason, the technique to which low temperature sintering of the dielectric ceramics is carried out is examined variously conventionally, and the three following large approaches are learned.

** How to form into the low melting point the liquid phase generation oxide of the approach ** dielectric which atomizes the temporary baking powder of the approach ** dielectric which adds glass [0003] Among these, although the effectiveness that the approach of ** to which the glassiness of the low melting point is added to dielectric materials, and sintering temperature is reduced makes sintering temperature low is high, a dielectric constant becomes low by adding glass to a dielectric presentation. Moreover, when glassiness with weak reinforcement is intermingled, there is a trouble that product reinforcement falls.

[0004] ** By atomizing the temporary baking powder of a dielectric with a medium agitation mill etc., an approach raises the reactivity of a particle, it is the approach of enabling baking at low temperature, for example, JP,7-277822,A, JP,8-104568,A, and JP,9-278535,A have a publication. However, generally the burning temperature of a PZT system ingredient is about 1200-1100 degrees C, and the width of face of the temperature which can carry out [low temperature]-izing by the approach of ** is at most about 100 degrees C. For example, in order to use cheap silver (Ag simple substance) as an electrode material, it is required for burning temperature to be 950 degrees C or less, and, also in the case of Ag containing Pd, 980 degrees C or less are required. Therefore, the approach of ** is not enough as the effectiveness which low-temperature-izes burning temperature.

[0005] ** An approach is the approach of forming into the low melting point the liquid phase generation oxide which forms the liquid phase at the time of baking of a dielectric. if PZT is mentioned as an example -- the presentation after temporary baking -- lead titanate (PbTiO₃), lead zirconate (PbZrO₃), and titanic-acid lead zirconate (it is the mixture of Pb(Ti0.5 Zr0.5) O₃, and participate in the generation reaction of PbTiO₃ and PbZrO₃ at the time of temporary baking -- slight PbO which was not forms the liquid phase at a baking process.) This liquid phase is PbTiO₃ one by one. PbZrO₃ It contacts and reacts and is Pb(Ti0.5Zr0.5) O₃. Low temperature sintering is made possible by thinking that baking progresses, adding the oxide which forms PbO into the low melting point in the preparation phase of raw material powder, and forming the liquid phase at low temperature more.

[0006]

[Problem(s) to be Solved by the Invention] however -- the approach of ** -- liquid phase generation oxide 3, i.e., PbTiO, PbZrO₃ participate in a generation reaction -- the amount of PbO which was not is uncontrollable. For this reason, the problem that sintering temperature changes by change of few manufacture conditions arises. Moreover, although liquid phase generation temperature changes with PbO at the time of baking, and the ratios of a low melting point oxide, since control of this ratio cannot be performed, sintering of a dielectric is uncontrollable to the temperature promoted effectively. Furthermore, although what is necessary is just to be in the grain boundary which is unrelated to a

dielectric presentation after the oxide to add calcinating, it may enter into a dielectric presentation, and when there are many amounts of residuals to a baking object, there is concern to which performance degradation poses a problem. [0007] this invention person etc. aims at preventing that control obtaining the dielectric ceramics in which baking at low temperature is possible, the amount of generation of the liquid phase, etc., make sintering temperature of a dielectric controllable, an additive moreover enters the dielectric organization after baking, and the engine performance of a dielectric is spoiled from before paying attention to the above-mentioned trouble. Moreover, the assistant oxide for obtaining such dielectric ceramics is realized, and it aims at manufacturing the dielectric of high performance with a sufficient controllability using this assistant oxide.

[0008]

[Means for Solving the Problem] Invention of claim 1 by this invention is ABO₃. When it has the dielectric ceramic presentation of a mold and B site is set to 1, it is the low-temperature baking-ized dielectric ceramics which uses as a principal component the constituent which contains the lead of 0.9 or more mole ratios to A site, and at least one sort in a tungsten and molybdenum is contained. The consistencies after the baking are 7.5 g/cm³. It is above, and when the content of the sum total of a tungsten and molybdenum sets lead to 1, it is characterized by being smaller than 0.37 mole ratios.

[0009] In the low-temperature baking-ized dielectric ceramics of this invention, a tungsten and molybdenum are added as an assistant oxide. If the dielectric ceramics is calcinated, these assistant oxide will reach the melting point around 730 degrees C to 980 degrees C, and will form the liquid phase during a ceramic presentation. The liquid phase offers the path of the mass transfer between ceramic particles, promotes the reaction between particles, and particle growth, and enables sintering at low temperature. A tungsten and molybdenum have an eutectic relation mutually in the state of the lead contained in the dielectric ceramics, and an oxide, and if the assistant oxide which consists of such mixture is used, since it can control liquid phase generation temperature by the blending ratio of coal and the amount of liquid phase generation can be controlled by the addition, control of sintering temperature becomes easy. Moreover, the liquid phase is extruded with particle growth to a grain boundary, moves between another particles, and if sintering of the ceramics progresses and it arrives at a sintered compact front face, it will be removed.

[0010] Therefore, sintering at low temperature is realized conventionally, and it is a consistency after baking 7.5 g/cm³. It can do highly with the above. Since it is easy to evaporate, there is a problem of the presentation change after baking, but lead is useful also as a leaden source of supply, if the effectiveness of making sintering temperature low and preventing presentation change is acquired and lead is added to an assistant oxide. Moreover, the ceramic performance degradation by the residual of an assistant oxide etc. can be controlled by specifying the content of the sum total of the tungsten and molybdenum to lead to 0.37 or less mole ratios. Furthermore, the completion of contraction at 980 degrees C or less enables use of inner layer electrodes of the low melting point, such as Ag-Pd, and Ag simple substance, Cu alloy, and can reduce cost.

[0011] In invention of claim 2, a tungsten and molybdenum are arranged in a grain boundary at high concentration rather than the inside of the grain of the dielectric ceramics. Since it is added as an assistant oxide and a tungsten and molybdenum exist mostly by the grain boundary, they can make effect on the dielectric engine performance small.

[0012] Claim 3 is invention of a laminating mold dielectric element, and has the laminated structure between which the electrode layer to which the melting point which uses copper as a principal component between the layers of the above-mentioned low-temperature baking-ized dielectric ceramics uses an electrode layer or silver thru/or silver, and palladium 1083 degrees C or less as a principal component was made to be placed. In using the dielectric ceramics of above-mentioned claims 1-3, coincidence sintering with the electrode layer of these low melting point is attained, and the manufacturing cost of a component can be reduced greatly.

[0013] Invention of claim 4 is the approach of manufacturing the above-mentioned low-temperature baking-ized dielectric ceramics, and uses the assistant oxide which blended at least one sort of oxide with the plumbic acid ghost at the following rate of a compounding ratio among a tungsten and molybdenum.

PbO_x+(WO₃ y+MoO₃ z)

however, x+y+z=1 and 0.005< y+z -- < -- 0.4, y, and z>=0 -- this assistant oxide -- ABO₃ the raw material mixture or the temporary-quenching object of the dielectric ceramics which uses as a principal component the constituent which contains the lead of 0.9 or more mole ratios to A site when it has the dielectric ceramic presentation of a mold and B site is set to 1 -- 0.05-mol % - 20-mol % -- it comes out comparatively, addition combination is carried out, and it mixes, fabricates and calcinates.

[0014] In a baking process, the assistant oxide of the above-mentioned combination reaches the melting point around 730 degrees C to 980 degrees C, and forms the liquid phase during a ceramic presentation. The liquid phase offers the path of the mass transfer between ceramic particles, promotes the reaction between particles, and particle growth, and

enables sintering at low temperature. By making the blending ratio of coal of PbO and (WO₃+MoO₃) into the above-mentioned range, by making liquid phase generation temperature low, and considering as the above-mentioned addition range, the assistant oxide of this invention controls the amount of liquid phase generation, and enables sintering at low temperature. The liquid phase is extruded with particle growth to a grain boundary, moves between another particles, and if sintering of the ceramics progresses and it arrives at a sintered compact front face, it will be removed.

[0015] Since the dielectric ceramics which added and calcinated the above-mentioned assistant oxide is sintered at the low temperature at which lead oxide does not evaporate and an assistant oxide hardly remains in a grain, desired dielectric characteristics are obtained. Especially, the effectiveness which makes sintering temperature low is acquired, an addition holding dielectric characteristics and reinforcement in the 0.05-20-mol range in which it is %. Moreover, when the above-mentioned assistant oxide is added to the temporary baking powder after temporary baking, control of the amount of the assistant oxide to temporary baking powder etc. becomes easy, and it is PbO and WO₃. Temporary baking powder is made to distribute to homogeneity the assistant oxide made into the predetermined ratio, and at desired temperature, the liquid phase can be made to be able to generate and it can calcinate with a more sufficient controllability.

[0016] The approach of claim 5 obtains at least one sort of oxide for the above-mentioned assistant oxide among a tungsten and molybdenum to a plumbic acid ghost dry type or by carrying out wet blending, or carrying out wet blending, and grinding, dry type or after carrying out temporary baking. PbO, and WO₃ and MoO₃ Although it is also good to have mixed each powder, if temporary quenching is carried out and it is the solid solution, the control stabilized more will be attained.

[0017] Let the amount of the lead raw material in the above-mentioned raw material mixture be the amount which reduced a supplied part from the lead oxide of the above-mentioned assistant oxide by the approach of claim 6 in the process which prepares the raw material mixture of the above-mentioned dielectric ceramics. Since the assistant oxide contains the lead oxide which constitutes the dielectric ceramics, if optimum dose ***** weighing capacity of a part to be supplied from an assistant oxide at the time of preparation of a raw material is carried out, lead oxide can all also reduce raw material cost superfluously to a sintered compact.

[0018] The approach of claim 7 uses for from the temperature used as 3% of self-contraction of the above-mentioned dielectric ceramics before the completion temperature of contraction the above-mentioned assistant oxide which has the melting point. In the phase where self-contraction of the dielectric ceramics used as a base material is small, when calcinating the Plastic solid in which the internal electrode etc. was formed, if the liquid phase by the assistant oxide generates, stress will join electrode material and exfoliation will arise. In order to prevent this, it is good to use an assistant oxide with the melting point beyond the temperature used as 3% of self-contraction, and it is making the liquid phase form by the completion temperature of contraction, and can calcinate effectively.

[0019] In case the approach of claim 8 fabricates the above-mentioned dielectric ceramics in the shape of a sheet, it uses the sheet which added the above-mentioned assistant oxide for the temporary baking powder which carried out temporary quenching of raw material powder or the raw material powder, is printed, carries out the laminating of the electrode layer to this, and does coincidence baking of it. If the above-mentioned assistant oxide is added as ** material to conductor material, the effectiveness of preventing stress joining electrode material and exfoliation arising by liquid phase generation will increase.

[0020] It comes to blend at least one sort of oxide with a plumbic acid ghost among a tungsten and molybdenum, and it is the assistant oxide used as an assistant at the time of sintering the ceramics, and invention of claim 9 has [the sum total content of a tungsten and molybdenum is larger than 0.5 mol %, and] it. [smaller than 40 mol %]

[0021] It is added by the dielectric ceramics, and the assistant oxide which blended (WO₃+MoO₃) with PbO at an above-mentioned rate makes liquid phase generation temperature low, and enables sintering at low temperature. Moreover, since the amount of liquid phase generation is controllable by the addition, control of burning temperature is easy and does not spoil the dielectric engine performance.

[0022] It comes to carry out temporary quenching of the mixture which blended at least one sort of oxide with the plumbic acid ghost among a tungsten and molybdenum, and the sum total content of a tungsten and molybdenum is larger than 0.5-mol %, and the assistant oxide of claim 10 has it. [smaller than 40 mol %] PbO and (WO₃+MoO₃) form the solid solution by temporary baking, and since the presentation is more uniform, it can distribute during a ceramic presentation, and the assistant oxide of claim 12 can form the liquid phase at desired temperature, and can advance sintering more effectively.

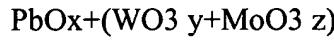
[0023]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. The low-temperature baking-ized dielectric ceramics of this invention is ABO₃. When it has the dielectric ceramic presentation of a mold and B site is set

to 1, while using as a principal component the constituent which contains the lead of 0.9 or more mole ratios to A site, at least one sort in a tungsten and molybdenum is contained. The constituent used as a principal component is specifically Pb(Ti, Zr) O₃. The PZT system ceramics which permuted the part by elements, such as Sr, Mn, Y, and Nb, is used suitably, and outstanding dielectric characteristics are shown. The concrete presentation of the blending ratio of coal of a permutation element or each component element etc. can be suitably chosen according to a required property. In addition, ABO₃ When the sum total of the component of A site containing lead sets B site to 1, it can also make A site for the dielectric ceramics of a mold to usually be blended so that it may become the mole ratio of A:B:O=1:1:3, but contain lead superfluously so that it may become 1.00 or more mole ratios. Since formation of the liquid phase in low temperature is made easy by making the lead of the low melting point superfluous and lead tends to evaporate, this is for preventing fluctuation of the presentation after baking.

[0024] By sintering the dielectric ceramics containing lead, such as PZT system ceramics, in this invention using the assistant oxide containing at least one sort in a tungsten and molybdenum, low-temperature baking is enabled and it is a consistency after baking 7.5 g/cm³ It considers as the above. It is made to become 0.30 or less mole ratios preferably so that it may become smaller than 0.37 mole ratios when the content of the sum total of the tungsten which needs to set up appropriately the amount of the tungsten which has a lead and eutectic relation in the state of oxide mutually in order to maintain the dielectric characteristics which acquired the effectiveness of the formation of low-temperature baking, and were excellent, and molybdenum, and is specifically contained in the dielectric ceramics after baking, and molybdenum sets lead to 1. Since a tungsten and molybdenum form the liquid phase, stimulate particle growth at the time of baking and are extruded by the grain boundary with particle growth, they are arranged in the grain boundary in the presentation after baking at high concentration rather than the inside of the grain of the dielectric ceramics.

[0025] An assistant oxide is used as an assistant at the time of sintering the dielectric ceramics, and comes to blend at least one sort in tungstic oxide (WO₃) and molybdenum oxide (MoO₃) with a lead oxide (PbO). WO₃ MoO₃ It is easy to be natural even if it adds both. WO₃ in an assistant oxide MoO₃ A total content is the larger range smaller than 40-mol % than 0.5-mol %, and is expressed with the following formulas.



However, $x+y+z=1$, $0.005 < y+z < 0.4$, y, and $z >= 0$ WO₃ MoO₃ A total content is [the melting point of a low melting point phase] 980 degrees C or more in range other than this, and the effectiveness of reducing the sintering temperature of a base material is not acquired.

[0026] What is necessary is to carry out weighing capacity of these powder, respectively, and just to mix preparation of an assistant oxide so that the blending ratio of coal of PbO and (WO₃+MoO₃) may serve as the above-mentioned range. Although dry blending may be used for mixing, wet blending performed by distributing water etc. is more desirable. Although it is usually desirable to use and grind a ball mill, a medium agitation mill, etc., and to atomize the particle size of mixed powder as for after mixing in order to raise reactivity, a grinding process is not necessarily required. Preferably, after grinding, temporary baking is performed at 270-730 degrees C, the temporary baking powder to which the part was made to react is obtained, and it considers as an assistant oxide. By performing temporary baking, the assistant oxide solid solution fused at request temperature is obtained, and the effectiveness which stabilizes liquid phase deposit temperature is acquired. The temporary baking powder of assistant oxide is further ground using a ball mill, a medium agitation mill, etc., and let it be a desired particle size. In addition, since, as for an assistant oxide, temporary baking advances after mixing with the dielectric ceramics, and during baking, it is not necessary to necessarily perform temporary baking in a preparation phase.

[0027] In this invention, in order to promote baking at the low temperature of the dielectric ceramics containing lead, such as PZT system ceramics, addition combination of the above-mentioned assistant oxide is carried out. Drawing 1 is the production process Fig. of the dielectric ceramics, and in case it mixes at the process of (2) after carrying out weighing capacity of the raw material compound of the dielectric ceramics at the process of (1), you may add and mix to coincidence, but if the mixed powder of (3) is added after the process which carries out temporary baking, since control of the amount of the assistant oxide to temporary baking powder etc. will become easy, an assistant oxide is more desirable. Usually perform temporary baking of the dielectric ceramics at 500-900 degrees C, and water, a binder, a dispersant, etc. are made to distribute the temporary baking powder obtained at the process of (4), and the pulverized powder of an assistant oxide is added, and it mixes and grinds. The addition of an assistant oxide is made into the 0.05-20-mol range of % to the obtained temporary baking powder, the effectiveness that an addition makes sintering temperature low less than [0.05 mol %] is not acquired, but if 20-mol % is exceeded, a consistency will fall. Sintering temperature can be made low so that there are many additions more than at 0.05 mol %, but when six-mol % is exceeded, it is desirable to consider as the 0.05-6-mol range of % suitably from firing time becoming long, in order to be in the inclination for reinforcement to fall and to acquire a required property. In addition, this addition is based on the

rate to the constituent after temporary baking also when adding an assistant oxide into the raw material powder of the dielectric ceramics.

[0028] After mixing the temporary baking powder and the assistant oxide of the dielectric ceramics, in the process of (5), after performing a granulation and drying by the usual approach, shaping and baking are performed at (6) or (7) process. Addition of an assistant oxide can also be performed into the granulation process of (5) besides in the grinding process of the temporary baking powder of the dielectric ceramics of (4). Although burning temperature is based on $\text{PbO}/(\text{WO}_3+\text{MoO}_3)$ ratio in an assistant oxide, and the addition of an assistant oxide, it is usually desirable in atmospheric air to carry out in 730-1100 degrees C. Moreover, at this time, it is desirable to arrange powder, such as a zirconium dioxide (ZrO_2) and lead zirconate (PbZrO_3), around a Plastic solid, and a reaction can remove the liquid phase product which came out to the front face after sintering.

[0029] By this invention, the assistant oxide which blended (WO_3+MoO_3) with PbO at a predetermined rate can be made into the condition that a desired low melting point liquid phase nucleus distributes during a PZT presentation, by adding at the time of temporary baking of the PZT system dielectric ceramics. If the mixture of this dielectric temporary baking powder and an assistant oxide is calcinated in air, an assistant oxide greets the melting point at the predetermined temperature of 730 degrees C or more, and it will be in the condition that the liquid phase exists in a lot of dielectric temporary baking powder at a minute amount. The liquid phase offers the path of mass transfer between particles, and generates a dielectric in response to mutual. Furthermore, the liquid phase promotes particle growth of a dielectric, is extruded with particle growth to a grain boundary, and moves between another particles. Drawing 2 is PbO-WO_3 . It is the state diagram of a system and is PbO and WO_3 . It has the melting point according to the blending ratio of coal, and is WO_3 . When [16.5 mol] it is %, what the melting point becomes the lowest (730 degrees C) is understood. WO_3 MoO_3 The same inclination is seen also when it replaces with.

[0030] Thus, the liquid phase can repeat a dielectric particle, contact, a reaction, particle growth, and migration, sintering can progress to the whole, and the PZT system dielectric ceramics can be made to sinter at the desired low temperature which evaporation of PbO does not produce by adjusting $\text{PbO}/(\text{WO}_3+\text{MoO}_3)$ ratio, and an addition. On the other hand, since it will react with ZrO , will be removed from a sintered compact, if the liquid phase reaches on the surface of a sintered compact, and it hardly remains during a sintered compact presentation, the effect on dielectric characteristics is small. Moreover, since Pb contained in a dielectric presentation is superfluously supplied from an assistant oxide, if optimum dose ***** preparation of the PbO which is the weighing capacity process of a dielectric raw material, and is equivalent to a part for the supply beforehand is carried out, since raw material cost is also controlled, PbO is all superfluously advantageous to a sintered compact. When the dielectric used as a principal component contains Pb superfluously, the optimum dose increase in quantity of the PbO is carried out conversely.

[0031] It calcinates, after fabricating the mixed powder of an assistant oxide and a dielectric in a predetermined configuration, carrying out printing formation and carrying out two or more laminatings of the conductor material used as an internal electrode to the obtained Plastic solid front face, in using for a piezoelectric transformer etc. the dielectric obtained as mentioned above. Since the melting point which low temperature sintering 980 degrees C or less is possible, and uses silver (Ag simple substance) cheap as a conductor material, and silver-palladium, copper or copper as a principal component by adjusting suitably a dielectric presentation, and $\text{PbO}/(\text{WO}_3+\text{MoO}_3)$ ratio of an assistant oxide, and an addition can use a copper alloy 1083 degrees C or less etc. at this time, a manufacturing cost can be reduced.

[0032] In addition, when carrying out coincidence baking of the layered product which has an inner conductor in this way, depending on the assistant oxide to be used, interlaminar peeling may arise after baking. Before self-contraction of a dielectric becomes 3%, this tends to happen, when a liquid phase nucleus occurs, and nonuniformity is made as for it to contraction according to uneven liquid phase nucleation, and it is considered for this to cause stress in an inner conductor side. So, in case an assistant oxide is chosen, it is good to choose a presentation which is in before the temperature which serves as a point completing [contraction] from the temperature which 3% of self-contraction of the dielectric with which the melting point serves as a base material completes, and generating of exfoliation can be prevented. Moreover, the same assistant oxide of a presentation can also be added as ** material into an inner conductor ingredient, and the prevention effectiveness of exfoliation can be heightened.

[0033]

[Example] Using the high grade powder of lead oxide and tungstic oxide as a raw material of an assistant oxide, weighing capacity was carried out so that the blending ratio of coal might become $\text{PbO}83.5 \text{ mol \%}: \text{WO}_3 16.5 \text{ mol \%}$. It is PbO and WO_3 by carrying out temporary baking at 500 degrees C among atmospheric air for 2 hours, after blending these dryly. The assistant oxide temporary-quenching powder (chemical formula-b0.835 WO 0.165O1.33) to which the part was made to react was obtained. The assistant oxide powder which atomized and dried this assistant oxide temporary-quenching powder with the medium agitation mill next, and raised reactivity was obtained.

[0034] On the other hand, as dielectric ceramics, the last presentation is $\{(Pb0.91Sr0.09) Zr0.538 Ti0.452 0.01(Y0.5 Nb0.5)\} O3+0.5atm\%Mn 2O3$. Weighing capacity of the high grade powder, such as the lead oxide and strontium oxide used as a raw material, a zirconium dioxide, titanium oxide, an oxidization yttrium, niobium oxide, and manganese oxide, was carried out so that it might become. After blending these ***** dryly, dielectric temporary baking powder was obtained among atmospheric air by carrying out temporary baking at 850 degrees C for 7 hours. Next, the dispersant (it is 2.5 % of the weight to dielectric temporary baking powder) was beforehand mixed with 2.5l. of water, in this mixture, 4.7kg of dielectric temporary baking powder was mixed gradually, and the dielectric temporary-quenching powder slurry was obtained. The pearl mill equipment which is a medium agitation mill was used, this dielectric temporary-quenching powder slurry was mixed, it ground, and particle diameter was controlled to 0.2 micrometers or less.

[0035] The weight of dielectric temporary baking powder is received [binder] in a release agent 4% of the weight to the weight of dielectric temporary baking powder to the dielectric temporary-quenching powder slurry under grinding with a medium agitation mill. 1.9 % of the weight, After mixing 13.5g (0.165O1.33:0.5 mol % of PbO0.835 WO(s)) for the assistant oxide which was able to be performed above to the weight of 1600g of derivative temporary baking powder and performing stirring for 3 hours, it dried with the spray dryer and the granulation powder of a dielectric temporary-quenching object was obtained. Shaping equipment is used for the obtained granulation powder, and it is 2 a 3.27g /cm] load to the diameter of 20mm, and the thickness of 1mm. The Plastic solid was acquired by fabricating.

[0036] The acquired Plastic solid was put into magnesia ***** , and optimum dose arrangement of the lead zirconate (PbZrO₃) was carried out, and it put into the perimeter in the firing furnace, it held at 950 degrees C among atmospheric air for 4 hours, and the dielectric sintered compact was obtained. This sintered compact was printed after lap processing, the silver paste was printed to both sides, and electrode baking was performed at 680 degrees C. Furthermore, what carried out periphery polish and made size the diameter of 13mm and the thickness of 0.5mm was polarized over 30 minutes by 130 degrees C and 0.9kV in the silicone oil, and the dielectric was obtained (sample 1).

[0037] The consistency of the obtained dielectric ceramics was 7.62 (g/cm³), and the piezoelectric constant d₃₁ was 1.51x10¹⁰ (m/V). With the base material which does not add an assistant oxide, it turns out with the burning temperature of 1050 degrees C that low-temperature baking is attained, a consistency holding high sintered density and a piezo-electric property, since 7.62 (g/cm³) and a piezoelectric constant d₃₁ are 1.62x10¹⁰ (m/V). Moreover, when the content of a tungsten in the dielectric ceramics was investigated, it was Pb:W=1:0.0004-0.0009 (mole ratio). A measuring method is [0038]. Moreover, it is WO₃ as a raw material of an assistant oxide. It is MoO₃ to instead of. Assistant oxide powder (chemical formula-b0.835 MoO 0.165O1.33) was obtained by the same approach except having used. It polarized and the dielectric was obtained, after having mixed 13.5g (0.5-mol %) to the weight of 1600g of the derivative temporary baking powder of the same presentation, having fabricated by the same approach, calcinating this assistant oxide by it and performing electrode baking (sample 2).

[0039] The consistency of the obtained dielectric ceramics was 7.64 (g/cm³), and the piezoelectric constant d₃₁ was 1.49x10¹⁰ (m/V). Moreover, when the content of molybdenum in the dielectric ceramics was investigated, it was Pb:Mo=1:0.0005-0.0015 (mole ratio). As mentioned above, also when it replaced with tungstic oxide and molybdenum oxide was adopted, it checked that same operation and effectiveness which forms the phase of the low melting point and promotes low temperature sintering were acquired.

[0040] Next, PbO and WO₃ of an assistant oxide It changed in the range which shows the blending ratio of coal in Table 1, and except having made the addition of an assistant oxide into three-mol %, it calcinated by the same approach as the above-mentioned sample 1, the relation between the blending ratio of coal and sintering temperature was investigated, and the result was indicated to Table 1. The TMA analyzer performed measurement of sintering temperature. It is WO₃ so that it may see in Table 1. Sintering temperature becomes low as loadings increase, and it is PbO/WO₃. It becomes low temperature most in the 83/17 neighborhood. WO₃ If the blending ratio of coal increases more than this, sintering temperature will rise again. It is WO₃ in order to acquire the effectiveness over the burning temperature (1050 degrees C) of a base material by addition of an assistant oxide. It turns out that the blending ratio of coal is larger than 0.5-mol %, and should be just smaller than 40%.

[0041]

[Table 1]

誘電体 +3mol%[(PbO)_{1-x}+(WO₃)_x] の焼結温度

| X | 焼結温度(°C) |
|-------|----------|
| 0 | 1050 |
| 0.005 | 1050 |
| 0.01 | 1010 |
| 0.03 | 990 |
| 0.17 | 920 |
| 0.25 | 1010 |
| 0.3 | 1030 |
| 0.4 | 1040 |
| 0.5 | 1100 |
| 0.665 | 970 |

[0042] Moreover, PbO and WO₃ of an assistant oxide It is PbO:83.5-mol % and WO₃ about the blending ratio of coal. : It presupposed that it is fixed at 16.5-mol %, the addition to a dielectric presentation was changed as shown in Table 2, it calcinated by the same approach as the above-mentioned sample 1, and the piezo-electric property was measured and it was indicated in Table 2 and Table 3 as the burning temperature from which sintered density equivalent to a base material (addition % of zero mol) is obtained. clear to Table 2 -- as -- an assistant oxide -- 0.02-mol % -- if it adds, from a base material, the effectiveness which makes burning temperature low will be seen and baking at 950 degrees C or less will be attained by 0.05-mol% of addition by 1000 degrees C or less, and 0.2-mol% of addition. Although burning temperature becomes low with the increment in an addition, when 20-mol % is exceeded from Table 3 here, sintered density is 7.50 (g/cm³). Since it is less and falls greatly, an addition is understood are good to consider as the 0.05-20-mol range of %.

[0043] Moreover, when the addition to the dielectric presentation of an assistant oxide measured the lead under dielectric presentation, and the ratio of a tungsten, respectively about the 20-mol sample it is [sample] % (sample 3), and the 25-mol % of sample (sample 4), the sample 3 was Pb:W=1:0.24 - 0.30 mole ratio, and the sample 4 was Pb:W=1:0.37 - 0.40 mole ratio.

[0044] As mentioned above, in order to acquire the effectiveness of this invention, it is required for the tungsten when setting lead to 1 and the mole ratio of the sum total of molybdenum to be smaller than 0.37, and it is good preferably in the mole ratio of the sum total of a tungsten and molybdenum being 0.30 or less.

[0045] In addition, although it is in the inclination for a piezoelectric constant to fall by the increment in an addition from Table 3, this is considered for burning temperature to be lower than a base material, and for a particle growth rate to fall. In such a case, when it is 0.5-mol % of an addition, as firing time can be lengthened and it can promote particle growth, for example, it is shown in Table 4, a base material, an EQC, or the piezo-electric property beyond it is acquired by lengthening firing time with 6 hours or 8 hours.

[0046]

[Table 2]

誘電体+Ymol%[(PbO)0.835+(WO₃)0.165]の特性

| Y | 密度(g/cm ³) 4H 焼成時 | 焼結温度(°C) |
|------|----------------------------------|----------|
| 0 | 7.62 | 1050 |
| 0.02 | 7.6 | 1020 |
| 0.05 | 7.6 | 1000 |
| 0.1 | 7.58 | 960 |
| 0.2 | 7.61 | 950 |
| 0.5 | 7.62 | 920 |
| 1 | 7.61 | 910 |
| 1.5 | 7.56 | 910 |
| 3 | 7.61 | 910 |
| 6 | 7.52 | 910 |
| 12 | 7.52 | 910 |
| 18 | 7.52 | 910 |
| 20 | 7.50 | 910 |
| 25 | 7.47 | 910 |

[0047]

[Table 3]

誘電体+Ymol%[(PbO)0.835+(WO₃)0.165]の特性

| Y | 密度(g/cm ³) 4H 焼成時 | 圧電定数d ₃₁ ×10 ¹⁰ (m/V) |
|------|----------------------------------|--|
| 0 | 7.62 | 1.62 |
| 0.02 | 7.6 | 1.62 |
| 0.05 | 7.6 | 1.6 |
| 0.1 | 7.58 | 1.58 |
| 0.2 | 7.61 | 1.55 |
| 0.5 | 7.62 | 1.51 |
| 1 | 7.61 | 1.47 |
| 1.5 | 7.56 | 1.38 |
| 3 | 7.61 | 1.12 |
| 6 | 7.52 | 0.64 |

母材

[0048]

[Table 4]

| 焼成時間 (H) | 密度 (g/cm ³) | 焼結温度 (°C) | 圧電定数d ₃₁ ×10 ¹⁰ (m/V) |
|-------------|----------------------------|--------------|--|
| 6 | 7.62 | 950 | 1.61 |
| 8 | 7.62 | 950 | 1.81 |

[0049] Furthermore, by preparing dielectric temporary baking powder by the same approach as the above-mentioned sample 1, adding an assistant oxide into the granulation powder, and fabricating using shaping equipment, as shown in drawing 4 (a), one piece of with four piece, and a thickness [the diameter of 20mm and thickness of 4mm] circular Plastic solid sheets 3 was prepared for the circular Plastic solid sheet 2 with a diameter [of 20mm], and a thickness of

1mm, and the laminating mold piezoelectric device 1 was manufactured using these. The procedure is explained below. First, as shown in drawing 4 (b), the internal electrode which consists of two printing patterns 4A and 4B was formed, the laminating of these was carried out to the upper front face of the Plastic solid sheet 2 of four piece by turns, and they were stuck to it by pressure. What formed Plastic solid 2A and printing pattern 4B for the thing in which printing pattern 4A was formed was shown as a Plastic solid 2B, using Ag paste as an internal electrode ingredient. The usual molding press performed sticking by pressure. It is at the inside of atmospheric air, and 950 degrees C about this layered product. After carrying out time amount baking, as shown in drawing 4 (a), the external electrodes 5A, 5B, and 5C were formed using Ag paste, and the laminating mold piezoelectric device 1 was obtained. Then, the lead wire which is not illustrated is given, polarization is given and it can use as a piezoelectric transformer.

[0050] Moreover, it can use as another application also as an electrostrictive actuator shown in drawing 5 (a). This comes to carry out the laminating of the Plastic solid sheets 11 and 12 of the rectangle shown in drawing 5 (c) like drawing 5 (d), and, in 113, the dummy section and 112 make the buffer section and 111 the mechanical component. In Plastic solid sheet 11 rectangular front face, printing formation of the electrode layer 41 or the electrode layer 42 from which a printing pattern differs except for the band-like section 119 has been carried out. Electrical installation serves as electric juxtaposition and a mechanical serial as it is shown in drawing 5 (b). The side-face electrodes 51 and 52 are applied, and the lead wire which is not illustrated is attached in this and it is made to act on it as an electrostrictive actuator, as shown in drawing 5 (a) and (b).

[0051] Here, the existence of interlaminar peeling after baking when changing various combination of the assistant oxide added into granulation powder was shown in Table 5. Under the present circumstances, two kinds of diameters of a primary particle of granulation powder were prepared, and the existence of interlaminar peeling in each particle diameter was shown. Moreover, the contraction curve in each particle diameter was shown in drawing 3. As shown in Table 5, exfoliation is easy to break out, so that particle diameter is still larger and contraction in low temperature is so small that the melting point of an assistant oxide is low. If the liquid phase occurs before 3% of self-contraction is completed although self-contraction of a dielectric occurs before the liquid phase karyogenesis by the assistant oxide from drawing 3 at the time of baking, it can be said that a rapid place and a loose place occur in contraction, this causes stress in an inner conductor side, and exfoliation is produced according to uneven liquid phase nucleation (based on temperature distribution). Therefore, in order to calcinate without exfoliation, in the contraction curve of drawing 3, it is good for the range to the temperature which serves as a point completing [contraction] from the temperature which 3% of self-contraction of a dielectric completes to choose based on the state diagram showing the assistant oxide presentation which has the melting point in drawing 2. a inner layer -- a conductor -- Ag-Pd -- when a conductor is used, generally burning temperature is about 980 degrees C, therefore the selection range of the assistant oxide in this case has become 40-mol % from 980-degree-C or less, i.e., 0.5 mol, %.

[0052]

Table 5

| | | 助剤酸化物 融点 (°C) | 830 | 730 | 800 | 900 |
|---------------|---------------------------------------|------------------|-----------|-------|-------|-----|
| 原料 粒径 (μm) | 組成 Pb ₂ WO ₆ | 90/10 | 83.5/16.5 | 78/22 | 70/30 | |
| 1.22 | ハクリの有無 | △ | × | △ | ○ | |
| | 溶融開始時の 自己収縮率 (%) | 2.5 | 0 | 1.6 | 6.2 | |
| 0.54 | ハクリの有無 | ○ | × | ○ | ○ | |
| | 溶融開始時の 自己収縮率 (%) | 3.8 | 1.4 | 3.2 | 8.2 | |

○ : ハクリなし
△ : ハクリ 5% 以下
× : ハクリ 5% 以上

[0053] Thus, without reducing the base material engine performance by choosing a suitable assistant oxide, low-temperature baking can be enabled, moreover interlaminar peeling of a layered product can be prevented, and the dielectric element of high performance can be obtained. Furthermore, when the same assistant oxide of a presentation was added into the inner conductor ingredient and the same laminating mold piezoelectric device 1 was manufactured, the incidence rate of exfoliation was able to be made lower.

[0054] In addition, in the above-mentioned example, although Ag was used for the inner conductor, the conductor which uses Cu as a principal component can also be used, and the same effectiveness is acquired. The example which manufactured the same laminating mold piezoelectric device 1 is shown below by using Cu as an inner conductor.

[0055] First, the assistant oxide powder added by the dielectric ceramics was prepared by the same approach as the above-mentioned sample 1 (chemical formula-b0.835 WO 0.165O1.33). Similarly, the last presentation is $\{(Pb0.91Sr0.09) Zr0.538 Ti0.452 0.01(Y0.5 Nb0.5)\} O_3 + 0.5atm\% Mn 2O_3$ as dielectric ceramics. So that it may become Mixing and the dielectric temporary-quenching powder slurry which carried out temporary baking, obtained dielectric temporary baking powder, and slurred this are received in raw material powder. the above-mentioned assistant oxide -- 0.5-mol % -- after adding and mixing (it is 13.5g to 1600g of dielectric temporary baking powder), it dried with the spray dryer and the granulation powder of a dielectric temporary-quenching object was obtained.

[0056] The solvent, the binder, the dispersant, etc. were added, and after atomizing and mixing with ball mill equipment, vacuum degassing was carried out to the obtained granulation powder one whole day and night. Then, it fabricated to the green sheet at intervals of [of 125 micrometers] the blade with doctor blade equipment. After drying at 80 degrees C, the sheet cutter cut the green sheet to 100mmx150mm, and it obtained the green sheet of the predetermined number of sheets of the same configuration.

[0057] subsequently, CuO paste (50 % of the weight [of CuO contents], and CuO specific-surface-area 10m²/g) 1800g -- receiving -- the Mitsui Mining & Smelting make (1050YP) -- after adding Cu powder:1.11g and ****:0.09g, it mixed with centrifugal-force stirring degassing equipment, and electrode paste was prepared. **** is the fine particles of the same presentation in the fine particles which consist of a part of component of the same presentation as dielectric materials, and dielectric materials, and is added by the purpose which doubles contraction with the purpose and electrode layer which improve the bond strength of an electrode layer and a dielectric layer, and a dielectric layer.

[0058] With screen-stencil equipment, after printing this electrode paste by the predetermined printing pattern with the thickness of 5-8 micrometers on the upper front face of each green sheet, it was dried at 130 degrees C for 1 hour. Furthermore, the 20-sheet (and green sheet which considers three layers of upper and lower sides at a time as sheet for dummies, and has not carried out electrode printing laminating) laminating of the green sheet which carried out electrode printing is carried out, it fixes to the fixture for sheet pressurization, and they are for 10 minutes and 80 kg/m² at 120 degrees C. Thermocompression bonding was carried out and the mother block was acquired. The sheet cutter cut the mother block which carried out thermocompression bonding to 9mmx9mm.

[0059] In addition, in this example, although the mother block was cut to 9mmx9mm, if it is more than 2mmx2mm, it is possible to acquire effectiveness with the application of this invention. Moreover, although laminating number of sheets was made into 20 sheets, number of sheets can be made arbitrary.

[0060] Next, they are for 10 minutes and 160 kg/m² at 120 degrees C with lamination equipment. Thermocompression bonding was carried out again and the layered product unit 62 of the dielectric sheet 61 shown in drawing 6 (a) and the internal electrode layer 7 was obtained. Here, the internal electrode layer 7 is arranged so that the electrode layer 71 of the printing pattern which an electrode exposes to a right lateral, and the electrode layer 72 of the printing pattern which an electrode exposes to a left lateral may be located by turns. The 20-piece laminating of this layered product unit 62 is carried out, and they are for 10 minutes and 500 kg/m² at 80 degrees C with lamination equipment. By carrying out thermocompression bonding again, the layered product 6 of the dielectric sheet 61 shown in drawing 6 (b) and the internal electrode layer 7 was obtained.

[0061] the condition of the obtained layered product 6 of having arranged the MgO plate 81 (15mmx15mmx1mm) of 20% of porosity up and down as shown in drawing 7 (a) -- MgO -- it put into the bowl like this, temperature control was carried out according to the cleaning pattern shown in drawing 7 (b) (500 degrees C of cleaning maximum temperatures), and it degreased in atmospheric air.

[0062] The layered product 6 which degreased performed reduction processing according to the reduction processing pattern of drawing 8 . In the ambient atmosphere containing Ar-H25000(1%) ml and O26.5(pure) -6ml, at the time of reduction, oxygen tension was managed by the oxygen tension outside a furnace, and it controlled to be set to 1x10-23.5 atm at this time. Moreover, processing temperature (maximum temperature) was made into about 350 degrees C, and was held at this temperature for 12 hours. Moreover, like the above-mentioned cleaning process, the MgO plate 81 has been arranged to the upper and lower sides of a layered product 1, it put into the bowl like this, and reduction processing was performed.

[0063] In addition, if the ambient atmosphere at the time of reduction processing can realize 1x10-14 - 1x10-25 atm by the oxygen tension outside a furnace, the concentration and throughput of gas will not be that limitation (at this time, the substantial ratio of H₂ and O₂ supplied in a furnace is H₂:O₂ =50:50-50:5.5). Processing temperature should be 305-400 degrees C, and the holding time should just be 0.25 - 16 hours.

[0064] the layered product 6 which performed reduction processing -- MgO -- it put in into the bowl like this and calcinated by reducing atmosphere. The fixture configuration in this case was shown in drawing 9 (a) and (b), has arranged the cordierite honeycomb object 83 to the upper and lower sides of a layered product 6 as the MgO plate 81 (15x15mmx1mm) and a spacer, respectively, and installed the MgO weight 82 (1-10g) in them at the topmost part. The appearance of the MgO weight 82 presupposed that it is almost the same as the MgO plate 81. Furthermore, in order to prevent PbO evaporating from a layered product 6 and changing a presentation like drawing 9 (c) at the time of an elevated temperature, optimum dose (it is 32g in total) arrangement of the lead zirconate (PbZrO₃) 84 was carried out like this at the base periphery section of a bowl.

[0065] It put into the furnace which can calcinate the bowl which will arrange and cook a layered product 6 as mentioned above by reducing atmosphere as shown in drawing 10 , and reduction baking was performed according to the temperature and the ambient atmosphere pattern shown in drawing 11 . Piping for introducing CO₂ (pure), Ar-CO (10%), and O₂ (pure) is connected to the furnace room like drawing 10 , and the flow can be controlled with a massflow controller, respectively.

[0066] The temperature up was carried out by the temperature and the ambient atmosphere pattern shown in drawing 11 (a), in the burning temperature of about 950 degrees C, and a furnace, by oxygen tension 1x10-6atm, it held for about 4 hours and the dielectric sintered compact was obtained. Thus, the profile when performing reduction baking came to be shown in drawing 11 (b), and has realized the ambient atmosphere by which less than 10y atm ($y=x^{**}0.3$) was stabilized to desired value x at the time of temperature and oxygen tension fixed.

[0067] In addition, not only above the temperature and the ambient atmosphere pattern of drawing 11 (a) but above 500 degrees C, it is temperature-partial pressure within the limits shown in drawing 11 (c), and reduction baking can also be performed, as shown in drawing, PbO is not returned but the same effectiveness is acquired by setting up the oxygen tension range where Cu does not oxidize according to burning temperature. At this time, it is CO₂. : It is desirable to be supplied all over a furnace by the ratio of CO:O₂ =5000:500-0:20-0. Moreover, about a programming rate, it is desirable to consider as the range of 300-20 degrees C/hour.

[Translation done.]

* NOTICES *

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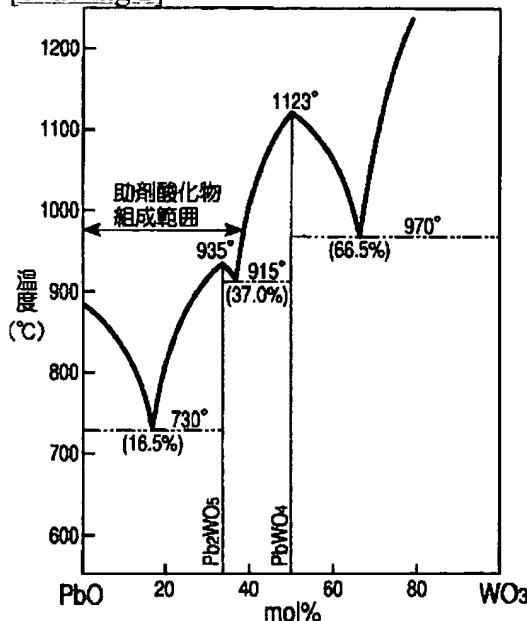
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2. *** shows the word which can not be translated.
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DRAWINGS

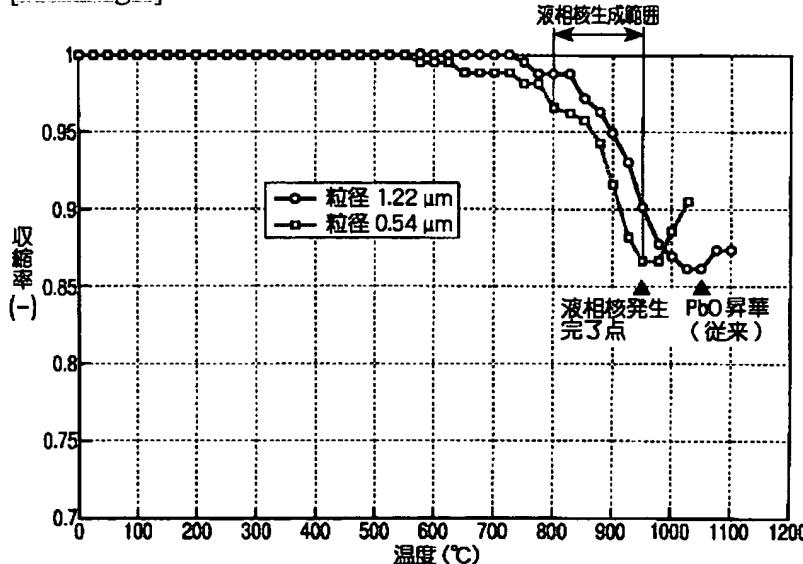
[Drawing 1]



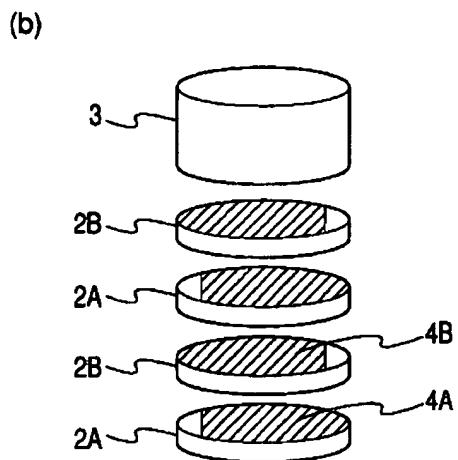
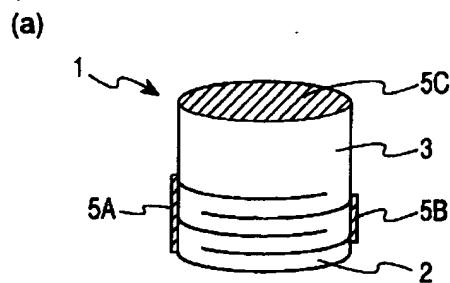
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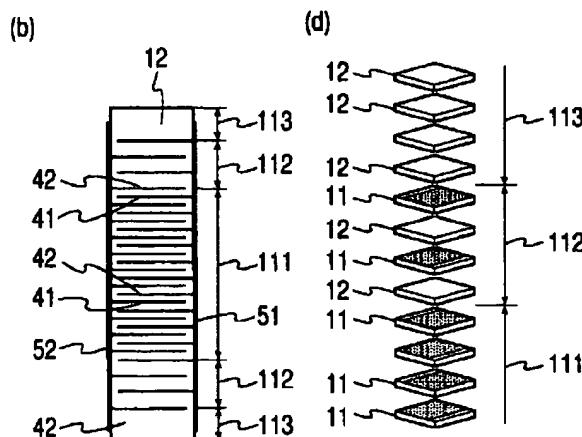
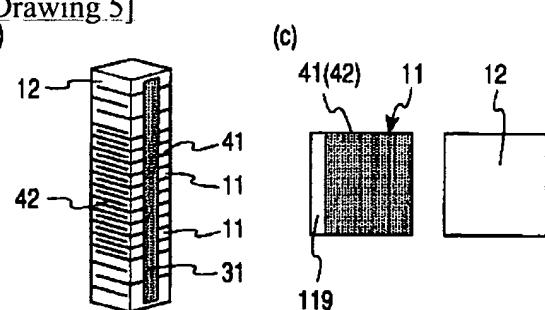
[Drawing 3]



[Drawing 4]

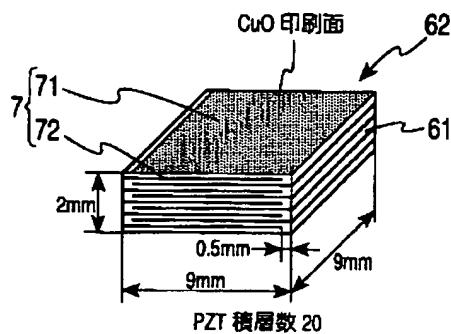


[Drawing 5]

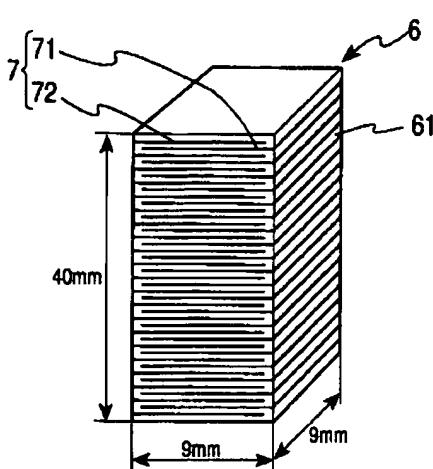


[Drawing 6]

(a)



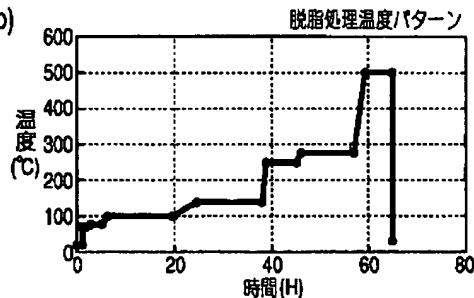
(b)



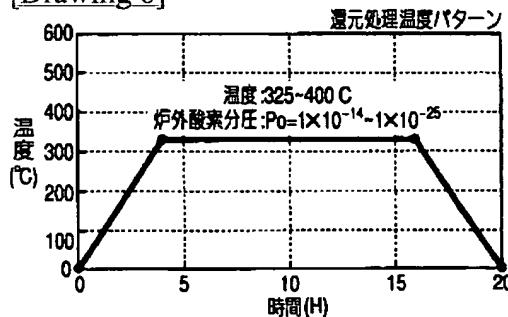
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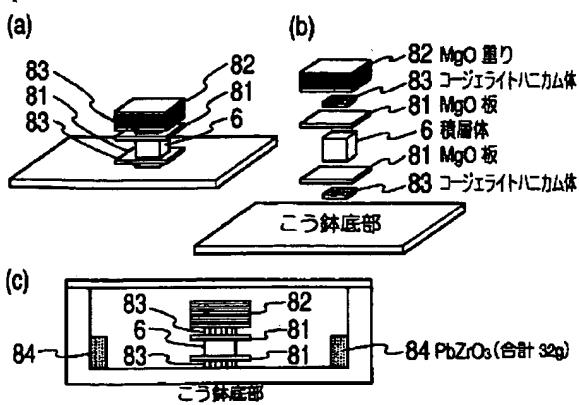
(b)



[Drawing 8]

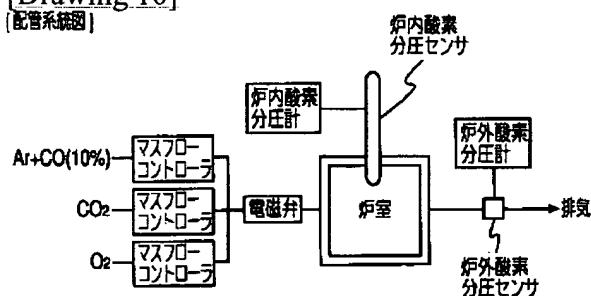


[Drawing 9]

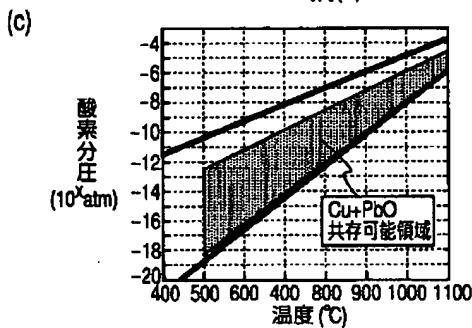
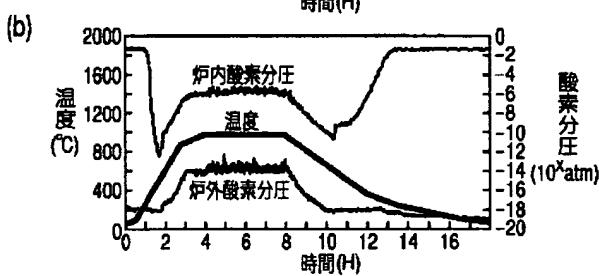
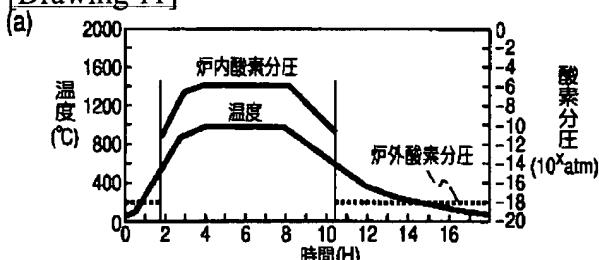


[Drawing 10]

[配管系統図]



[Drawing 11]



[Translation done.]

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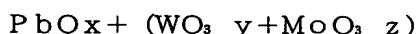
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(54)【発明の名称】低温焼成化誘電体セラミックス、積層型誘電体素子、誘電体セラミックスの製造方法および助剤酸化物

(57)【要約】

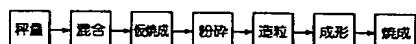
【課題】 P Z T 系誘電体セラミックスを所望の低温で焼成可能とし、かつ母材の性能が損なわれることを防止する。

【解決手段】 ABO₃ 型の誘電体セラミックス組成を有し、B サイトを 1 とした時に、A サイトに 0. 9 モル比以上の鉛を含有する組成物を主成分とする誘電体セラミックスの原料混合物または仮焼物に、助剤酸化物として、



ただし、 $x + y + z = 1$ 、 $0.005 < y + z < 0.4$ 、 $y, z \geq 0$

を 0.05 モル%～20 モル%の割合で添加配合し、混合、成形、焼成する。焼成体中のタンゲステンとモリブデンの合計の含有量は、鉛を 1 とした時に 0.098 モル比より小さく、焼成後の密度は 7.5 g / cm³ 以上となる。助剤酸化物は仮焼成粉中に分散して、所望の温度で液相を形成して焼成を促進し、低温焼成を可能にする。



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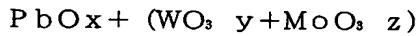
【特許請求の範囲】

【請求項1】 ABO_3 型の誘電体セラミックス組成を有し、Bサイトを1とした時に、Aサイトに0.9モル比以上の鉛を含有する組成物を主成分とするとともに、タンゲステンおよびモリブデンのうち少なくとも1種を含有し、焼成後の密度が7.5 g/cm³以上で、かつタンゲステンとモリブデンの合計の含有量が、鉛を1とした時に0.37モル比より小さいことを特徴とする低温焼成化誘電体セラミックス。

【請求項2】 タンゲステンおよびモリブデンが、誘電体セラミックスの粒内よりも粒界において高濃度に配置されている請求項1記載の低温焼成化誘電体セラミックス。

【請求項3】 上記請求項1または2のいずれか記載の低温焼成化誘電体セラミックスの層間に、銅を主成分とする融点が1083℃以下の電極層、または、銀ないし銀とパラジウムを主成分とする電極層を介在させた積層構造を有する積層型誘電体素子。

【請求項4】 上記請求項1または2のいずれか記載の低温焼成化誘電体セラミックスを製造する方法であつて、鉛酸化物に、タンゲステンおよびモリブデンのうち少なくとも1種の酸化物を下記の配合比率で配合した助剤酸化物を用い、



ただし、 $x + y + z = 1$ 、 $0.005 < y + z < 0.4$ 、 $y, z \geq 0$

ABO_3 型の誘電体セラミックス組成を有し、Bサイトを1とした時に、Aサイトに0.9モル比以上の鉛を含有する組成物を主成分とする誘電体セラミックスの原料混合物または仮焼物に、上記助剤酸化物を0.05モル%～20モル%の割合で添加配合し、混合、成形、焼成することを特徴とする誘電体セラミックスの製造方法。

【請求項5】 上記助剤酸化物を、鉛酸化物にタンゲステンおよびモリブデンのうち少なくとも1種の酸化物を乾式または湿式混合するか、あるいは、乾式または湿式混合し、仮焼成した後、粉碎することにより得る請求項4記載の誘電体セラミックスの製造方法。

【請求項6】 上記誘電体セラミックスの原料混合物を調合する工程において、上記原料混合物中の鉛原料の量を、上記助剤酸化物の酸化鉛からの供給分を減じた量とする請求項4または5記載の誘電体セラミックスの製造方法。

【請求項7】 上記誘電体セラミックスの自己収縮率3%となる温度から収縮完了温度までの間に融点を有する上記助剤酸化物を用いる請求項4ないし6のいずれか記載の誘電体セラミックスの製造方法。

【請求項8】 上記誘電体セラミックスをシート状に成形する際、原料粉または原料粉を仮焼した仮焼成粉に上記助剤酸化物を添加したシートを用いて、これに電極層を印刷、積層し、同時焼成する請求項5ないし7のいず

れか記載の誘電体セラミックスの製造方法。

【請求項9】 セラミックスを焼結する際の助剤として用いられる助剤酸化物であつて、鉛酸化物に、タンゲステンおよびモリブデンのうち少なくとも1種の酸化物を配合してなり、タンゲステンおよびモリブデンの合計含有量が0.5モル%より大きく40モル%より小さいことを特徴とする助剤酸化物。

【請求項10】 セラミックスを焼結する際の助剤として用いられる助剤酸化物であつて、鉛酸化物に、タンゲステンおよびモリブデンのうち少なくとも1種の酸化物を配合した混合物を仮焼してなり、タンゲステンおよびモリブデンの合計含有量が0.5モル%より大きく40モル%より小さいことを特徴とする助剤酸化物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、鉛を組成中に含む誘電体セラミックス、特に低温焼結が可能な誘電体セラミックスとその製造方法、および低温焼結を可能とするための助剤酸化物に関する。

【0002】

【従来の技術】 P Z T (チタン酸ジルコン酸鉛) 系の誘電体セラミックスは、圧電トランジスタ、圧電アクチュエータ等の材料として有用であるが、焼成温度が高温であると、酸化鉛 (PbO) が蒸発して所望の焼結体組成が得られないおそれがある、内部電極材料として高価な白金 (Pt) 等の高融点金属を使用する必要がありコスト高となる、といった不具合がある。このため、誘電体セラミックスを低温焼結させる技術が、従来より、種々検討されており、大きく下記の3つの方法が知られている。

① ガラスを添加する方法

② 誘電体の仮焼成粉を微粒化する方法

③ 誘電体の液相生成酸化物を低融点化する方法

【0003】 このうち、誘電体材料に低融点のガラス質を添加して焼結温度を低下させるの方法は、焼結温度を低くする効果は高いが、誘電体組成にガラスを添加することによって誘電率が低くなる。また、強度の弱いガラス質が混在すると、製品強度が低下するといった問題点がある。

【0004】 ②の方法は、誘電体の仮焼成粉を媒体攪拌ミル等で微粒化することにより、粒子の反応性を向上させ、低温での焼成を可能にする方法で、例えば、特開平7-277822号公報、特開平8-104568号公報、特開平9-278535号公報に記載がある。しかしながら、一般にP Z T系材料の焼成温度は1200～1100℃程度であり、②の方法により低温化できる温度の幅は、高々100℃程度である。例えば、安価な銀 (Ag単体) を電極材料として使用するには、焼成温度が950℃以下であることが必要であり、また、Pdを含むAgの場合にも980℃以下が必要である。従つて、②の方法では、焼成温度を低温化する効果が十分で

はない。

【0005】③の方法は、誘電体の焼成時に液相を形成する液相生成酸化物を低融点化する方法である。P Z Tを例に挙げると、仮焼成後の組成は、チタン酸鉛($PbTiO_3$)とジルコン酸鉛($PbZrO_3$)とチタン酸ジルコン酸鉛($Pb(Ti_{0.5}Zr_{0.5})O_3$)の混合物となっており、仮焼成時に $PbTiO_3$ と $PbZrO_3$ の生成反応に与かれなかった僅かな PbO が、焼成工程で液相を形成する。この液相が順次 $PbTiO_3$ と $PbZrO_3$ に接触、反応して、 $Pb(Ti_{0.5}Zr_{0.5})O_3$ の焼成が進むと考えられ、原料粉末の調合段階で、 PbO を低融点化する酸化物を添加し、より低温で液相を形成することにより、低温焼結を可能にしている。

【0006】

【発明が解決しようとする課題】しかしながら、③の方法では、液相生成酸化物、すなわち $PbTiO_3$ と $PbZrO_3$ の生成反応に与かれなかった PbO の量を制御できない。このため、僅かな製造条件の変化で焼結温度が変化するという問題が生じる。また、焼成時の PbO と低融点酸化物の比によって液相生成温度が変化するが、この比の制御ができないために、誘電体の焼結を効果的に促進する温度に制御できない。さらに、添加する酸化物が焼成後に誘電体組成と関係のない粒界にあればよいが、誘電体組成に入り込む可能性があり、焼成体への残留量が多いと性能の低下が問題となる懸念がある。

【0007】本発明者等は、上記問題点に着目し、従来より低温での焼成が可能な誘電体セラミックスを得ること、かつ、液相の生成量等を制御して誘電体の焼結温度を制御可能とし、しかも焼成後の誘電体組織に添加物が入り込んで誘電体の性能が損なわれるのを防止することを目的とする。また、このような誘電体セラミックスを得るための助剤酸化物を実現し、そして、この助剤酸化物を用いて制御性よく高性能の誘電体を製造することを目的とする。

【0008】

【課題を解決するための手段】本発明による請求項1の発明は、 ABO_3 型の誘電体セラミックス組成を有し、Bサイトを1とした時に、Aサイトに0.9モル比以上の鉛を含有する組成物を主成分とする低温焼成化誘電体セラミックスで、タンゲステンおよびモリブデンのうち少なくとも1種を含有する。その焼成後の密度は7.5g/cm³以上であり、かつタンゲステンとモリブデンの合計の含有量が、鉛を1とした時に0.37モル比より小さいことを特徴とする。

【0009】本発明の低温焼成化誘電体セラミックスにおいて、タンゲステンとモリブデンは、助剤酸化物として添加される。誘電体セラミックスの焼成を行うと、これら助剤酸化物が730℃から980℃前後で融点に達し、セラミックス組成中に液相を形成する。液相はセラ

ミックス粒子間の物質移動の経路を提供し、粒子間の反応、粒子成長を促進して、低温での焼結を可能にする。タンゲステンとモリブデンは、誘電体セラミックスに含まれる鉛と酸化物の状態で互いに共晶関係にあり、これらの混合物からなる助剤酸化物を用いると、その配合割合によって液相生成温度を、また、その添加量によって液相生成量を制御することができるので、焼結温度の制御が容易になる。また、液相は粒子成長とともに粒界へ押し出されて、別の粒子間に移動し、セラミックスの焼結が進んで焼結体表面に達すると取り除かれる。

【0010】よって、従来より低温での焼結を実現し、かつ焼成後の密度を7.5g/cm³以上と高くできる。鉛は蒸発しやすいので、焼成後の組成変化の問題があるが、焼結温度を低くして組成変化を防止する効果が得られ、助剤酸化物に鉛を添加すれば、鉛の供給源としても有用である。また、鉛に対するタンゲステンとモリブデンの合計の含有量を0.37モル比以下に規定することで、助剤酸化物の残留等によるセラミックス性能の低下を抑制することができる。さらに、980℃以下の収縮完了は、Ag-Pdや、Ag単体、Cu合金等の低融点の内層電極の使用を可能とし、コストが低減できる。

【0011】請求項2の発明において、タンゲステンおよびモリブデンは、誘電体セラミックスの粒内よりも粒界において高濃度に配置される。タンゲステンおよびモリブデンは助剤酸化物として添加されて、粒界により多く存在するため、誘電体性能への影響を小さくできる。

【0012】請求項3は積層型誘電体素子の発明で、上記低温焼成化誘電体セラミックスの層間に、銅を主成分とする融点が1083℃以下の電極層、または、銀ないし銀とパラジウムを主成分とする電極層を介在させた積層構造を有する。上記請求項1～3の誘電体セラミックスを用いることでは、これら低融点の電極層との同時焼結が可能になり、素子の製造コストを大きく低減できる。

【0013】請求項4の発明は、上記低温焼成化誘電体セラミックスを製造する方法であって、鉛酸化物に、タンゲステンおよびモリブデンのうち少なくとも1種の酸化物を下記の配合比率で配合した助剤酸化物を用いる。

40 $PbO_x + (WO_3 y + MoO_3 z)$

ただし、 $x + y + z = 1$ 、 $0.005 < y + z < 0.4$ 、 $y, z \geq 0$

この助剤酸化物を、 ABO_3 型の誘電体セラミックス組成を有し、Bサイトを1とした時に、Aサイトに0.9モル比以上の鉛を含有する組成物を主成分とする誘電体セラミックスの原料混合物または仮焼物に、0.05モル%～20モル%の割合で添加配合し、混合、成形、焼成する。

【0014】焼成工程において、上記配合の助剤酸化物50 は、730℃から980℃前後で融点に達し、セラミッ

クス組成中に液相を形成する。液相はセラミックス粒子間の物質移動の経路を提供し、粒子間の反応、粒子成長を促進して、低温での焼結を可能にする。本発明の助剤酸化物は、 PbO と $(WO_3 + MoO_3)$ の配合割合を上記範囲とすることによって液相生成温度を低くし、また、上記添加量範囲とすることによって液相生成量を制御して、低温での焼結を可能とする。液相は粒子成長とともに粒界へ押し出されて、別の粒子間に移動し、セラミックスの焼結が進んで焼結体表面に達すると取り除かれる。

【0015】上記助剤酸化物を添加して焼成した誘電体セラミックスは、酸化鉛が蒸発しない低温で焼結され、かつ助剤酸化物が粒内にほとんど残留しないので、所望の誘電特性が得られる。特に、添加量が0.05～20モル%の範囲で、誘電特性や強度を保持しつつ焼結温度を低くする効果が得られる。また、仮焼成後の仮焼成粉に対して上記助剤酸化物を添加すると、仮焼成粉に対する助剤酸化物の量の制御等が容易になり、 PbO と WO_3 を所定比とした助剤酸化物を仮焼成粉に均一に分散させ、所望の温度で液相を生成させて、より制御性よく焼成を行うことができる。

【0016】請求項5の方法は、上記助剤酸化物を、鉛酸化物にタンクステンおよびモリブデンのうち少なくとも1種の酸化物を乾式または湿式混合するか、あるいは、乾式または湿式混合し、仮焼成した後、粉碎することにより得る。 PbO と WO_3 、 MoO_3 は各粉末を混合しただけでもよいが、仮焼して固溶体とするとより安定した制御が可能になる。

【0017】請求項6の方法では、上記誘電体セラミックスの原料混合物を調合する工程において、上記原料混合物中の鉛原料の量を、上記助剤酸化物の酸化鉛からの供給分を減じた量とする。助剤酸化物が誘電体セラミックスを構成する酸化鉛を含んでいるので、原料の調合時に助剤酸化物から供給される分を適量減じて秤量すれば、酸化鉛が焼結体に過剰に残らず、原料コストも低減できる。

【0018】請求項7の方法は、上記誘電体セラミックスの自己収縮率3%となる温度から収縮完了温度までの間に融点を有する上記助剤酸化物を用いる。内部電極等を形成した成形体を焼成する場合、母材となる誘電体セラミックスの自己収縮率が小さい段階で、助剤酸化物による液相が生成すると、電極材に応力が加わって剥離が生じてしまう。これを防止するには、自己収縮率3%となる温度以上の融点を持つ助剤酸化物を用いるのがよく、かつ収縮完了温度までに液相を形成させることで、効果的に焼成を行うことができる。

【0019】請求項8の方法は、上記誘電体セラミックスをシート状に成形する際、原料粉または原料粉を仮焼した仮焼成粉に上記助剤酸化物を添加したシートを用いて、これに電極層を印刷、積層し、同時焼成する。導体

材料に上記助剤酸化物を共材として添加すると、液相生成により、電極材に応力が加わって剥離が生じるのを防止する効果が高まる。

【0020】請求項9の発明は、セラミックスを焼結する際の助剤として用いられる助剤酸化物で、鉛酸化物に、タンクステンおよびモリブデンのうち少なくとも1種の酸化物を配合してなり、タンクステンおよびモリブデンの合計含有量が0.5モル%より大きく40モル%より小さいものである。

10 【0021】 PbO と $(WO_3 + MoO_3)$ を上記割合で配合した助剤酸化物は、誘電体セラミックスに添加されて、液相生成温度を低くし、低温での焼結を可能とする。また、添加量によって液相生成量を制御できるので、焼成温度の制御が容易で、誘電体性能を損なうこともない。

【0022】請求項10の助剤酸化物は、鉛酸化物に、タンクステンおよびモリブデンのうち少なくとも1種の酸化物を配合した混合物を仮焼してなり、タンクステンおよびモリブデンの合計含有量が0.5モル%より大きく40モル%より小さいものである。請求項12の助剤酸化物は、仮焼成により PbO と $(WO_3 + MoO_3)$ が固溶体を形成しており、組成がより均一であるので、セラミックス組成中に分散して所望の温度で液相を形成し、より効果的に焼結を進めることができる。

【0023】
【発明の実施の形態】以下、本発明を詳細に説明する。本発明の低温焼成化誘電体セラミックスは、 ABO_3 型の誘電体セラミックス組成を有し、Bサイトを1とした時に、Aサイトに0.9モル比以上の鉛を含有する組成物を主成分とするとともに、タンクステンおよびモリブデンのうち少なくとも1種を含有する。主成分となる組成物は、具体的には $Pb(Ti, Zr)O_3$ や、その一部を Sr 、 Mn 、 Y 、 Nb 等の元素と置換した PZT 系セラミックスが好適に用いられ、優れた誘電特性を示す。置換元素や各成分元素の配合割合等、具体的な組成は必要な特性に応じて適宜選択することができる。なお、 ABO_3 型の誘電体セラミックスは、通常、A:B:O=1:1:3のモル比となるように配合されるが、鉛を含むAサイトの成分の合計が、Bサイトを1とした時に、1.00モル比以上となるように、Aサイトに鉛を過剰に含有させることもできる。これは、低融点の鉛を過剰にすることで低温での液相の形成を容易にする、また、鉛が蒸発しやすいことから焼成後の組成の変動を防ぐためである。

【0024】本発明では、 PZT 系セラミックス等の鉛を含有する誘電体セラミックスを、タンクステンおよびモリブデンのうち少なくとも1種を含有する助剤酸化物を用いて焼結することにより、低温焼成を可能にし、焼成後の密度を 7.5 g/cm^3 以上とする。低温焼成化の効果を得、かつ優れた誘電特性を維持するには、互い

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に酸化物の状態で鉛と共に晶関係にあるタンゲステンおよびモリブデンの量を適切に設定する必要があり、具体的には、焼成後の誘電体セラミックス中に含有されるタンゲステンおよびモリブデンの合計の含有量が、鉛を1とした時に0.37モル比より小さくなるように、好ましくは、0.30モル比以下となるようにする。タンゲステンおよびモリブデンは、焼成時に液相を形成して粒子成長を促し、粒子成長に伴い粒界に押し出されるため、焼成後の組成においては、誘電体セラミックスの粒内よりも粒界において高濃度に配置されている。

【0025】助剤酸化物は、誘電体セラミックスを焼結する際の助剤として用いられるもので、酸化鉛(PbO)に酸化タンゲステン(WO₃)および酸化モリブデン(MoO₃)のうち少なくとも1種を配合してなる。WO₃とMoO₃の両方を添加してももちろんよい。助剤酸化物中のWO₃とMoO₃の合計の含有量は、0.5モル%より大きく4.0モル%より小さい範囲であり、以下の式で表される。

$$PbO_x + (WO_3 y + MoO_3 z)$$

ただし、 $x + y + z = 1$ 、 $0.005 < y + z < 0.5$

4. $y, z \geq 0$

WO₃とMoO₃の合計の含有量が、これ以外の範囲では低融点相の融点が980℃以上であり、母材の焼結温度を低下させる効果が得られない。

【0026】助剤酸化物の調製は、PbOと(WO₃ + MoO₃)の配合割合が上記範囲となるように、これらの粉末をそれぞれ秤量し、混合すればよい。混合は乾式混合でもよいが、水等に分散させて行う湿式混合がより望ましい。混合後は、通常、反応性を高めるために、ボールミルや媒体攪拌ミル等を用いて粉碎し、混合粉の粒径を微粒化することが望ましいが、粉碎工程は必ずしも必要ではない。好ましくは、粉碎後に、270~730℃で仮焼成を行い、その一部を反応させた仮焼成粉を得て、助剤酸化物とする。仮焼成を行うことで、所望温度で溶融する助剤酸化物固溶体を得、液相析出温度を安定化する効果が得られる。助剤酸化物の仮焼成粉は、さらにボールミルや媒体攪拌ミル等を用いて粉碎し、所望の粒径とする。なお、助剤酸化物は、誘電体セラミックスと混合後、焼成中に仮焼成が進行するため、必ずしも調製段階での仮焼成は行わなくてもよい。

【0027】本発明では、PZT系セラミックス等の鉛を含有する誘電体セラミックスの、低温での焼成を促進するために、上記助剤酸化物を添加配合する。図1は誘電体セラミックスの製造工程図で、助剤酸化物は、

(1)の工程で誘電体セラミックスの原料化合物を秤量した後、(2)の工程で混合する際に、同時に添加、混合してもよいが、(3)の混合粉を仮焼成する工程の後に添加すると、仮焼成粉に対する助剤酸化物の量の制御等が容易になるので、より好ましい。誘電体セラミックスの仮焼成は、通常、500~900℃で行い、(4)

の工程で得られた仮焼成粉を水、バインダー、分散剤等に分散させ、助剤酸化物の粉碎粉を添加して、混合、粉碎する。助剤酸化物の添加量は、得られた仮焼成粉に対して0.05~2.0モル%の範囲とし、添加量が0.05モル%未満では、焼結温度を低くする効果が得られず、2.0モル%を越えると密度が低下する。0.05モル%以上で添加量が多いほど焼結温度を低くすることができるが、6モル%を越えると、強度が低下する傾向があり、必要な特性を得るために焼成時間が長くなることから、好適には、0.05~6モル%の範囲とすることが好ましい。なお、この添加量は、助剤酸化物を誘電体セラミックスの原料粉に添加する場合も、仮焼成後の組成物に対する割合を基準とする。

【0028】誘電体セラミックスの仮焼成粉と助剤酸化物を混合後、(5)の工程において、通常の方法で造粒を行い、乾燥した後、(6)、(7)の工程で成形、焼成を行う。助剤酸化物の添加は、(4)の誘電体セラミックスの仮焼成粉の粉碎工程中の他、(5)の造粒工程中に行うこともできる。焼成温度は、助剤酸化物中のPbO/(WO₃ + MoO₃)比と、助剤酸化物の添加量によるが、通常、大気中で、730~1100℃の範囲で行なうことが望ましい。また、この時、成形体の周囲に酸化ジルコニウム(ZrO₂)、ジルコン酸鉛(PbZrO₃)等の粉末を配置しておくことが望ましく、焼結後に表面に出てきた液相生成物を反応により除去することができる。

【0029】本発明では、PbOに(WO₃ + MoO₃)を所定の割合で配合した助剤酸化物を、PZT系誘電体セラミックスの仮焼成時に添加することで、PZT組成中に所望の低融点液相核が分散することができる。この誘電体仮焼成粉と助剤酸化物の混合物を空気中で焼成すると、730℃以上の所定の温度にて助剤酸化物が融点を迎え、多量の誘電体仮焼成粉の中に液相が微量に存在する状態となる。液相は粒子間で物質移動の経路を提供するものであり、相互に反応して誘電体を生成する。さらに液相は誘電体の粒子成長の促進をし、粒子成長とともに粒界へ押し出されて、別の粒子間に移動する。図2は、PbO-WO₃系の状態図で、PbOとWO₃の配合割合に応じた融点を有し、WO₃が

16.5モル%の時に融点が最も低くなる(730℃)ことがわかる。WO₃をMoO₃にえた場合にも同様の傾向が見られる。

【0030】このように、液相が誘電体粒子と接触、反応、粒子成長、移動を繰り返して全体に焼結が進み、PbO/(WO₃ + MoO₃)比や添加量を調整することで、PbOの蒸発が生じない所望の低温でPZT系誘電体セラミックスを焼結させることができる。一方、液相は焼結体の表面に達すると、ZrOと反応して焼結体より取り除かれ、焼結体組成中にほとんど残留しないので、誘電特性への影響が小さい。また、誘電体組成に含

まれるPbが助剤酸化物から過剰に供給されるため、誘電体原料の秤量工程で、予め、その供給分に相当するPbOを適量減じて調合すれば、PbOが過剰に焼結体に残らず、原料コストも抑制されるので有利である。主成分となる誘電体がPbを過剰に含む場合には、逆に、PbOを適量増量する。

【0031】上記のようにして得られる誘電体を圧電トランジス等に用いる場合には、助剤酸化物と誘電体の混合粉を所定の形状に成形し、得られた成形体表面に内部電極となる導体材料を印刷形成して、複数積層した後、焼成する。この時、誘電体組成や、助剤酸化物のPbO/(WO₃ + MoO₃)比、添加量を適宜調整することで、980°C以下の低温焼成が可能であり、導体材料として安価な銀(Ag単体)や銀-パラジウム、銅または銅を主成分とする融点が1083°C以下の銅合金等を使用することができるので、製造コストが低減できる。

【0032】なお、このように、内部導体を有する積層体を同時焼成する場合、使用する助剤酸化物によっては、焼成後に層間剥離が生じることがある。これは、誘電体の自己収縮率が3%となる前に、液相核が発生する場合に起こりやすく、不均一な液相核形成によって収縮にムラができ、これが内部導体面に応力を引き起こすためと考えられる。そこで、助剤酸化物を選択する際には、融点が、母材となる誘電体の3%の自己収縮が完了する温度から収縮完了点となる温度までの間にあるような組成を選ぶとよく、剥離の発生を防止することができる。また、同じ組成の助剤酸化物を、内部導体材料と共に材として添加することもでき、剥離の防止効果を高めることができる。

【0033】

【実施例】助剤酸化物の原料として酸化鉛と酸化タンゲステンの高純度粉末を用い、配合割合がPbO 83.5モル% : WO₃ 16.5モル%となるように秤量した。これらを乾式混合した後、大気中、500°Cで2時間仮焼成することで、PbOとWO₃の一部を反応させた助剤酸化物仮焼粉(化学式:Pb_{0.835}WO_{0.165}O_{1.33})を得た。この助剤酸化物仮焼粉を、次に媒体攪拌ミルにより微粒化、乾燥して反応性を高めた助剤酸化物粉を得た。

【0034】一方、誘電体セラミックスとしては、最終組成が(Pb_{0.91} Sr_{0.09})₂(Zr_{0.538} Ti_{0.452}(Y_{0.5} Nb_{0.5})_{0.01})O₃ + 0.5atm% Mn₂O₃となるように、原料となる酸化鉛、酸化ストロンチウム、酸化ジルコニウム、酸化チタン、酸化イットリウム、酸化ニオブ、酸化マンガン等の高純度粉末を秤量した。これら粉末を乾式混合した後、大気中、850°Cで7時間仮焼成することで、誘電体仮焼成粉を得た。次に、水2.5リットルと分散剤(誘電体仮焼成粉に対して2.5重量%)を予め混合しておき、この混合物中に、誘電体仮焼成粉4.7kgを徐々に混合して誘

電体仮焼粉スラリーを得た。この誘電体仮焼粉スラリーを媒体攪拌ミルであるパールミル装置を用いて、混合、粉碎し、粒子径を0.2μm以下に制御した。

【0035】媒体攪拌ミルで粉碎中の誘電体仮焼粉スラリーに対して、バインダを誘電体仮焼成粉の重量に対して4重量%、離型剤を誘電体仮焼成粉の重量に対して1.9重量%と、上記のようにして得た助剤酸化物を、誘導体仮焼成粉の重量1600gに対して13.5g(PbO_{0.835}WO_{0.165}O_{1.33}:0.5モル%)を混合し、3時間攪拌を行った後、スプレードライヤで乾燥して、誘電体仮焼成粉の造粒粉を得た。得られた造粒粉を成形装置を用いて、直径20mm、厚み1mmに、荷重3.27g/cm²で成形することにより、成形体を得た。

【0036】得られた成形体をマグネシアこう鉢にいれ、その周囲にジルコン酸鉛(PbZrO₃)を適量配置して焼成炉に入れ、大気中、950°Cで4時間保持して、誘電体焼結体を得た。この焼結体をラップ処理後、銀ペーストを両面に印刷し、680°Cで電極焼き付けを行った。さらに、外周研磨してサイズを直径13mm、厚み0.5mmとしたものを、シリコンオイル中で130°C、0.9kVで30分かけて分極して、誘電体を得た(試料1)。

【0037】得られた誘電体セラミックスは、密度が7.62(g/cm³)であり、圧電定数d₃₁は1.51×10¹⁰(m/V)であった。助剤酸化物を添加しない母材では、焼成温度1050°Cで、密度が7.62(g/cm³)、圧電定数d₃₁は1.62×10¹⁰(m/V)であるので、高い焼結密度と圧電特性を保持しつつ、低温焼成が可能になることがわかる。また、誘電体セラミックス中の、タンゲステンの含有量を調べたところ、Pb:W=1:0.0004~0.0009(モル比)であった。測定方法は、

【0038】また、助剤酸化物の原料としてWO₃の代わりにMoO₃を用いた以外は、同様の方法で助剤酸化物粉(化学式:Pb_{0.835}MoO_{0.165}O_{1.33})を得た。この助剤酸化物を、同一組成の誘導体仮焼成粉の重量1600gに対して13.5g(0.5モル%)を混合し、同様の方法で成形、焼成し、電極焼き付けを行った後、分極して、誘電体を得た(試料2)。

【0039】得られた誘電体セラミックスは、密度が7.64(g/cm³)であり、圧電定数d₃₁は1.49×10¹⁰(m/V)であった。また、誘電体セラミックス中の、モリブデンの含有量を調べたところ、Pb:Mo=1:0.0005~0.0015(モル比)であった。以上より、酸化タンゲステンに代えて酸化モリブデンを採用した場合も、低融点の相を形成して低温焼結を促進する同様の作用・効果が得られることを確認した。

【0040】次に、助剤酸化物のPbOとWO₃の配合

割合を表1に示す範囲で変更し、助剤酸化物の添加量を3モル%とした以外は、上記試料1と同様の方法で焼成を行って、配合割合と焼結温度の関係を調べて、結果を表1に記載した。焼結温度の測定はTMA分析器によつて行った。表1に見られるように、 WO_3 の配合量が増すにつれて焼結温度が低くなり、 PbO/WO_3 が8.3/1.7付近で最も低温となる。 WO_3 の配合割合がこれより多くなると再び焼結温度が上昇する。助剤酸化物の添加によって母材の焼成温度(1050°C)に対する効果を得るには、 WO_3 の配合割合が0.5モル%より大きく、4.0%より小さければよいことがわかる。

【0041】

【表1】

誘電体+3mol%[(PbO) $_{1-x}$ +(WO_3) $_x$]の焼結温度

| X | 焼結温度(°C) |
|-------|----------|
| 0 | 1050 |
| 0.005 | 1050 |
| 0.01 | 1010 |
| 0.03 | 990 |
| 0.17 | 920 |
| 0.25 | 1010 |
| 0.3 | 1030 |
| 0.4 | 1040 |
| 0.5 | 1100 |
| 0.665 | 970 |

鉛を1とした時のタンゲステンとモリブデンの合計のモル比が0.37より小さいことが必要であり、好ましくは、タンゲステンとモリブデンの合計のモル比が0.30以下であるとよい。

【0045】なお、表3より添加量の増加によって圧電定数が低下する傾向にあるが、これは、母材よりも焼成温度が低く粒子成長速度が低下するためと考えられる。

このような場合には、焼成時間を長くして粒子成長を促進することができ、例えば、0.5モル%の添加量の場合、表4に示すように、焼成時間を6時間または8時間と長くすることで、母材と同等ないしそれ以上の圧電特性が得られる。

【0046】

【表2】

誘電体+Ymol%[(PbO) $_{0.835}$ +(WO_3) $_{0.165}$]の特性

| Y | 密度(g/cm ³) 4H焼成時 | 焼結温度(°C) |
|------|---------------------------------|----------|
| 0 | 7.62 | 1050 |
| 0.02 | 7.6 | 1020 |
| 0.05 | 7.6 | 1000 |
| 0.1 | 7.58 | 960 |
| 0.2 | 7.61 | 950 |
| 0.5 | 7.62 | 920 |
| 1 | 7.61 | 910 |
| 1.5 | 7.56 | 910 |
| 3 | 7.61 | 910 |
| 6 | 7.52 | 910 |
| 12 | 7.52 | 910 |
| 18 | 7.52 | 910 |
| 20 | 7.50 | 910 |
| 25 | 7.47 | 910 |

【0042】また、助剤酸化物のPbOと WO_3 の配合割合をPbO:8.3.5モル%、 WO_3 :16.5モル%で一定とし、誘電体組成への添加量を表2のように変更して、上記試料1と同様の方法で焼成を行い、母材

(添加量0モル%)と同等の焼結密度が得られる焼成温度と、圧電特性を測定して表2、表3に示した。表2に明らかなように、助剤酸化物を0.02モル%添加すれば、母材より焼成温度を低くする効果が見られ、0.05モル%の添加で1000°C以下、0.2モル%の添加で950°C以下での焼成が可能になる。ここで、添加量の増加に伴い焼成温度が低くなるが、表3より20モル%を越えると焼結密度が7.50(g/cm³)を下回り大きく低下するので、添加量は0.05~20モル%の範囲とするといふことがわかる。

【0043】また、助剤酸化物の誘電体組成への添加量が20モル%の試料(試料3)と、25モル%の試料(試料4)について、それぞれ誘電体組成中の鉛とタンゲステンの比を測定したところ、試料3はPb:W=1:0.24~0.30モル比、試料4はPb:W=1:0.37~0.40モル比であった。

【0044】以上より、本発明の効果を得るためには、

【0047】

【表3】

誘電体+Ymol%[(PbO)_{0.835}+(WO₃)_{0.165}]の特性

| Y | 密度(g/cm ³) 4H 焼成時 | 圧電定数d ₃₁ ×10 ¹⁰ (m/V) |
|------|----------------------------------|--|
| 0 | 7.62 | 1.62 |
| 0.02 | 7.6 | 1.62 |
| 0.05 | 7.6 | 1.6 |
| 0.1 | 7.58 | 1.58 |
| 0.2 | 7.61 | 1.55 |
| 0.5 | 7.62 | 1.51 |
| 1 | 7.61 | 1.47 |
| 1.5 | 7.56 | 1.38 |
| 3 | 7.61 | 1.12 |
| 6 | 7.52 | 0.64 |

母材

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【0048】

【表4】

| 焼成時間 (H) | 密度 (g/cm ³) | 焼結温度 (°C) | 圧電定数d ₃₁ ×10 ¹⁰ (m/V) |
|-------------|----------------------------|--------------|--|
| 6 | 7.62 | 950 | 1.61 |
| 8 | 7.62 | 950 | 1.81 |

【0049】さらに、上記試料1と同じ方法で誘電体仮焼成粉を調製し、その造粒粉に助剤酸化物を添加して、成形装置を用いて成形することにより、図4 (a) に示すように、直徑20mm、厚み1mmの円形の成形体シート2を4ピースと、直徑20mm、厚み4mmの円形の成形体シート3を1ピース準備し、これらを用いて積層型圧電素子1を製作した。その手順を以下に説明する。まず、図4 (b) に示すように、4ピースの成形体シート2の上表面に、2つの印刷パターン4A、4Bからなる内部電極を形成して、これらを交互に積層し、圧着した。内部電極材料としてはAgペーストを用い、印刷パターン4Aを形成したものを成形体2A、印刷パターン4Bを形成したものを成形体2Bとして示した。圧着は、通常の成形プレスにて行った。この積層体を大気中、950°Cにて時間焼成した後、図4 (a) に示すように、外部電極5A、5B、5CをAgペーストを用いて形成して、積層型圧電素子1を得た。その後、図示しないリード線を付与して分極を施し、圧電トランジストとして利用できる。

【0050】また、別の用途として、図5 (a) に示す圧電アクチュエータとしても用いることができる。これは、図5 (c) に示す矩形の成形体シート11、12を、図5 (d) の如く積層してなり、113はダミー部、112はバッファ一部、111を駆動部としている。矩形の成形体シート11表面には、帯状部119を除いて印刷パターンの異なる電極層41または電極層42が印刷形成してある。電気的接続は、図5 (b) に示

す通り、電気的並列かつ機械的直列となっている。これに、図5 (a)、(b) に示されるように、側面電極51、52を塗布し、図示しないリード線を取付け、圧電アクチュエータとして作用させる。

【0051】ここで、造粒粉に添加した助剤酸化物の配合を種々変化させた時の、焼成後の層間剥離の有無を表5に示した。この際、造粒粉の一次粒子径を2種類準備して、それぞれの粒子径での層間剥離の有無を示した。また、各粒子径における収縮率曲線を図3に示した。表5のように、剥離は助剤酸化物の融点が低いほど、さらに粒子径が大きく低温での収縮率が小さいほど、起きやすくなっている。図3から、焼成時には、助剤酸化物による液相核発生前に、誘電体の自己収縮が発生するが、3%の自己収縮が完了する前に液相が発生すると、不均一な液相核形成(温度分布による)によって収縮に急激なところと緩やかなところが発生し、これが内部導体面に応力を引き起こして剥離を生じさせるといえる。よつて、剥離なく焼成するには、図3の収縮率曲線において、誘電体の3%の自己収縮が完了する温度から収縮完了点となる温度までの範囲に、融点を有する助剤酸化物組成を、図2に示す状態図を基に選択するとよい。内層導体にAg-Pd導体を使用した場合、一般的に焼成温度は980°C程度であり、従って、この場合の助剤酸化物の選択範囲は、980°C以下、つまり、0.5モル%から40モル%となっている。

【0052】

【表5】

| 原料 粒径(μm) | 助剤酸化物 組成 Pb _{0.835} WO _{0.165} O _{1.33} | 助剤酸化物 融点(℃) | | | |
|--------------|--|----------------|-----|-----|-----|
| | | 830 | 730 | 800 | 900 |
| 1.22 | ハクリの有無 | △ | × | △ | ○ |
| | 溶融開始時の 自己吸収率(%) | 2.5 | 0 | 1.6 | 6.2 |
| 0.54 | ハクリの有無 | ○ | × | ○ | ○ |
| | 溶融開始時の 自己吸収率(%) | 3.8 | 1.4 | 3.2 | 8.2 |

○:ハクリなし
△:ハクリ5%以下
×:ハクリ5%以上

【0053】このように、適切な助剤酸化物を選択することにより、母材性能を低下させることなく、低温焼成を可能にし、しかも積層体の層間剥離を防止して、高性能の誘電体素子を得ることができる。さらに、同じ組成の助剤酸化物を、内部導体材料に添加して、同様の積層型圧電素子1を製作したところ、剥離の発生率をより低くすることができた。

【0054】なお、上記実施例では、内部導体にAgを使用したが、Cuを主成分とする導体を用いることもでき、同様の効果が得られる。Cuを内部導体として、同様の積層型圧電素子1を製作した実施例を以下に示す。

【0055】まず、上記試料1と同様の方法で、誘電体セラミックスに添加される助剤酸化物粉を調製した(化学式:Pb_{0.835}WO_{0.165}O_{1.33})。同様に、誘電体セラミックスとして、最終組成が(Pb_{0.91}Sr_{0.09}{Zr_{0.538}Ti_{0.452}(Y_{0.5}Nb_{0.5})_{0.01}}O₃+0.5atm%Mn₂O₃)となるように、原料粉末を混合、仮焼成して誘電体仮焼成粉を得、これをスラリー化した誘電体仮焼成粉スラリーに対して、上記助剤酸化物を0.5モル%添加、混合した(誘電体仮焼成粉1600gに対して13.5g)後、スプレードライヤで乾燥して、誘電体仮焼成粉を得た。

【0056】得られた造粒粉に、溶媒、バインダ、分散剤等を添加して、一昼夜ボールミル装置にて、微粒化、混合した後、真空脱泡した。その後、ドクターブレード装置により、ブレード間隔125μmでグリーンシートに成形した。グリーンシートは80℃で乾燥した後、シートカッターで100mm×150mmに切断し、同一形状の所定枚数のグリーンシートを得た。

【0057】次いで、CuOペースト(CuO含有量50重量%、CuO比表面積10m²/g)1800gに対して三井金属(株)製(1050YP)Cu粉:1.11gおよび共粉:0.09gを添加した後、遠心力攪拌脱泡装置により混合して、電極ペーストを調製した。共粉は、誘電体材料と同じ組成か、誘電体材料の成分の一部からなる粉体で同じ組成の粉体で、電極層と誘電体層の接着強度を向上する目的および電極層と誘電体層と

の収縮を合わせ込む目的に添加される。

【0058】この電極ペーストを、スクリーン印刷装置により、各グリーンシートの上表面に5~8μmの厚みで、所定の印刷パターンにて印刷した後、130℃で1時間乾燥した。さらに、電極印刷したグリーンシートを20枚(および上下3層づつダミー用シートとして電極印刷していないグリーンシートを積層)積層して、シート加圧用治具に固定し、120℃で10分間、80kg/m²で熱圧着してマザーブロックを得た。熱圧着したマザーブロックは、シートカッターで9mm×9mmに切断した。

【0059】なお、本実施例では、マザーブロックを9mm×9mmに切断したが、2mm×2mm以上であれば、本発明を適用して効果を得ることが可能である。また、積層枚数を20枚としたが、枚数は任意とすることができます。

【0060】次に、ラミネート装置にて、120℃で10分間、160kg/m²で再び熱圧着して、図6(a)に示す誘電体シート61と内部電極層7の積層体ユニット62を得た。ここで、内部電極層7は、右側面に電極が露出する印刷パターンの電極層71と、左側面に電極が露出する印刷パターンの電極層72が交互に位置するように配置される。この積層体ユニット62を20個積層し、ラミネート装置にて、80℃で10分間、500kg/m²で再び熱圧着することにより、図6(b)に示す誘電体シート61と内部電極層7の積層体6を得た。

【0061】得られた積層体6の上下に、図7(a)に示すように、気孔率20%のMgO板81(15mm×15mm×1mm)を配置した状態で、MgOこう鉢にいれ、図7(b)に示す脱脂パターンに従って温度制御して(脱脂最高温度500℃)、大気中で脱脂を行った。

【0062】脱脂した積層体6は、図8の還元処理パターンに従い、還元処理を行った。この時、Ar-H₂(1%)5000mlおよびO₂(pure)6500mlを含む雰囲気中で、還元時酸素分圧を、炉外

酸素分圧で管理して、 $1 \times 10^{-23.5}$ atmとなるように制御した。また、処理温度（最高温度）は約350℃とし、この温度で12時間保持した。また、上記脱脂工程と同様に、積層体1の上下にMgO板81を配置して、こう鉢に入れて還元処理を行った。

【0063】なお、還元処理時の雰囲気は、炉外酸素分圧で $1 \times 10^{-14} \sim 1 \times 10^{-26}$ atmを実現できれば、ガスの濃度および処理量はその限りではない（この時、炉内に投入する実質的なH₂とO₂の比は、H₂ : O₂ = 50 : 50 ~ 50 : 5.5）。処理温度は、305~400℃、保持時間は、0.25~16時間の間であればよい。

【0064】還元処理を行った積層体6を、MgOこう鉢中に入れ、還元雰囲気で焼成した。この際の治具構成は、図9（a）、（b）に示すようにし、積層体6の上下に、MgO板81（15×15mm×1mm）およびスペーサとしてコーチェライトハニカム体83をそれぞれ配置し、最上部には、MgO重り82（1~10g）を設置した。MgO重り82の外形は、MgO板81とほぼ同じとした。さらに、図9（c）のように、高温時に積層体6からPbOが蒸発して組成が変動するのを防止するため、こう鉢の底面外周部にジルコン酸鉛（PbZrO₃）84を適量（合計で32g）配置した。

【0065】上記のように積層体6を配置したこう鉢を、図10に示すような、還元雰囲気で焼成可能な炉に入れ、図11に示す温度・雰囲気パターンに従って還元焼成を行った。図10のように、炉室には、CO₂（pure）、Ar-CO（10%）およびO₂（pure）を導入するための配管が接続されており、それぞれマスフローコントローラで流量調整可能となっている。

【0066】図11（a）に示す温度・雰囲気パターンで昇温して、焼成温度約950℃、炉内酸素分圧 1×10^{-6} atmで、約4時間保持して、誘電体焼結体を得た。このようにして、還元焼成を行った時のプロファイルは、図11（b）に示すようになり、温度・酸素分圧一定時において、目標値xに対して 10^y （y=x±0.3）atm以内の安定した雰囲気が実現できた。

【0067】なお、図11（a）の温度・雰囲気パターンに限らず、500℃以上では、図11（c）に示す温度一分圧範囲内で還元焼成を行うこともでき、図のよう

に、PbOが還元されず、Cuが酸化されない酸素分圧範囲を、焼成温度に応じて設定することで、同様の効果が得られる。この時、CO₂ : CO : O₂ = 5000 : 500~0 : 20~0の比で炉中に投入されることが望ましい。また、昇温速度については、300~20℃/時間の範囲とすることが望ましい。

【図面の簡単な説明】

【図1】誘電体セラミックスの製造工程図である。

【図2】PbO-WO₃二元系状態図である。

【図3】誘電体の焼成時の収縮率曲線を示す図である。

【図4】（a）は本発明の誘電体を用いた積層型圧電素子の概略構成図、（b）は（a）の分解斜視図である。

【図5】（a）は本発明の誘電体を用いた圧電アクチュエータの全体斜視図、（b）は圧電アクチュエータの電気的接続を示す概略構成図、（c）は圧電アクチュエータを構成するシートの正面図、（d）は圧電アクチュエータの分解斜視図である。

【図6】（a）は積層体ユニット、（b）は積層体ユニットを重ねて得た積層体の概略構成を示す斜視図である。

【図7】（a）は脱脂工程における治具構成を示す展開斜視図、（b）は脱脂処理温度パターンを示す図である。

【図8】還元処理温度パターンを示す図である。

【図9】（a）は焼成工程における治具構成を示す斜視図、（b）、（c）は（a）の展開斜視図、側面図である。

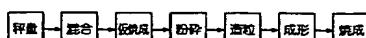
【図10】焼成工程における焼成炉構成と配管系統を示す図である。

【図11】（a）は目標とする温度・酸素分圧パターンを示す図、（b）は実際の温度・酸素分圧パターンを示す図、（c）はCuの酸化およびPbOの還元が生じる温度-酸素分圧の関係を示す図である。

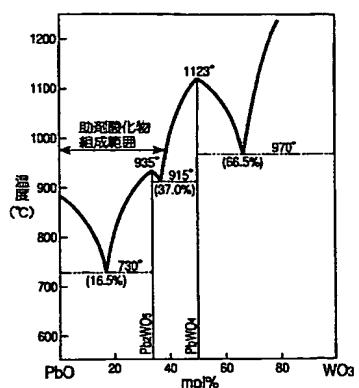
【符号の説明】

- 1 積層型圧電素子
- 2、2A、2B 成形体シート
- 3 成形体シート
- 4A、4B 印刷パターン
- 5A、5B、5C 外部電極

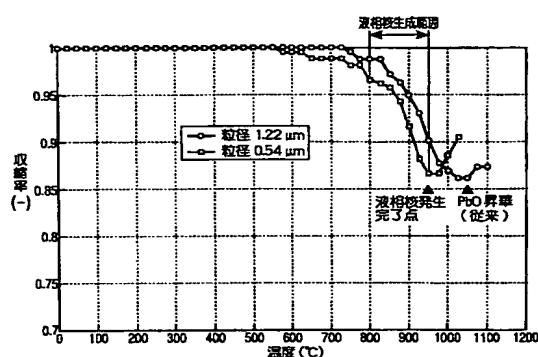
【図1】



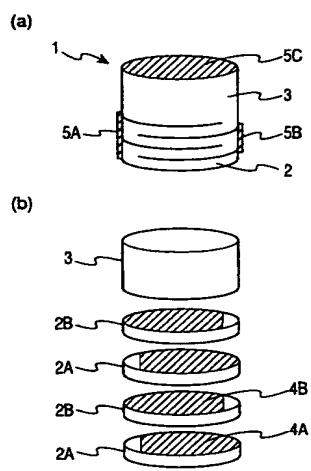
【図2】



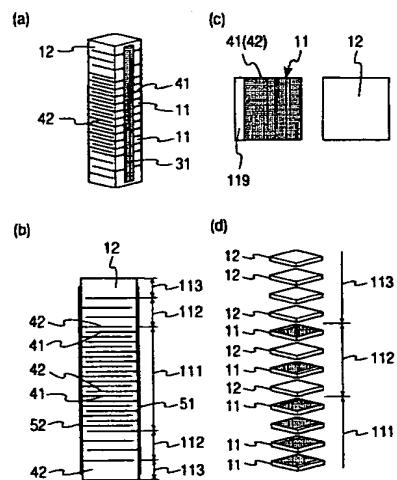
【図3】



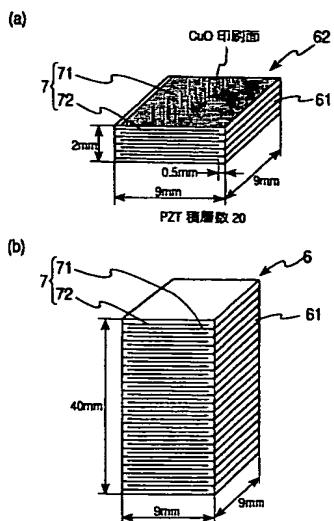
【図4】



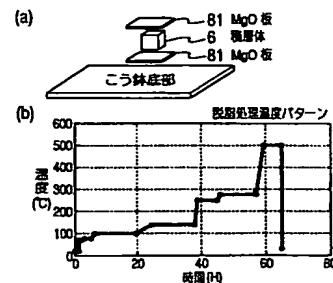
【図5】



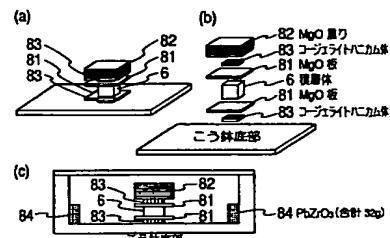
【図6】



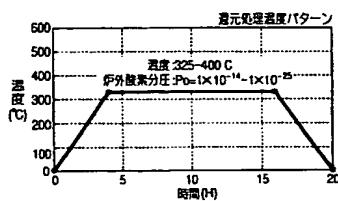
【図7】



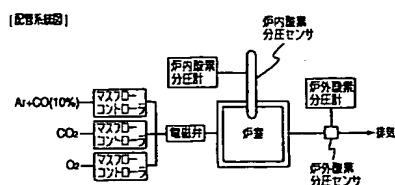
【図9】



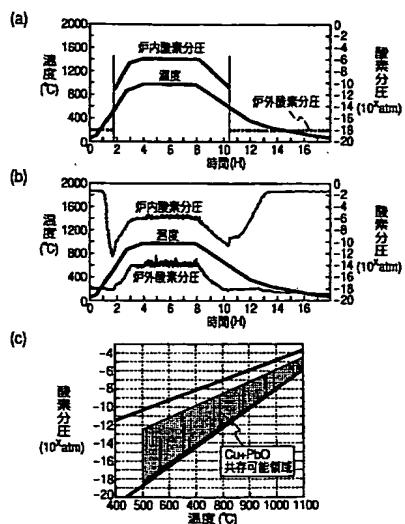
【図8】



【図10】



【図11】



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CB21 CB25 CB32 CB35 CB37

CB39 CB40 CB43 CC03 CD01

CD04 DA05

It is an object of this invention to provide a high dielectric constant porcelain composition that has a large dielectric constant as well as a low temperature coefficient that is capable of being baked at a low temperature 1100 °C or less, and that is outstanding at moistureproof-loading tests when used as a laminating ceramic condenser.

The present invention provides a high dielectric constant porcelain composition comprising a porcelain composition and 0.01~1.0 wt% of at least one member selected from the group consisting of oxidized silver Ag_2O , oxidized palladium PdO and oxidized platinum PtO ,

wherein said porcelain composition is obtained by replacing a part of Pb in the formulation, $x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - y\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - z\text{PbTiO}_3$, with 1~35 mol% of one or both of Ba and Sr,

wherein said formulation lies within the joining lines of the points

- a (x=0.50, y=0.00, z=0.50),
- b (x=1.00, y=0.00, z=0.00),
- c (x=0.20, y=0.80, z=0.00) and
- d (x=0.05, y=0.90, z=0.05)

of the ternary phase diagram in which $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, PbTiO_3 are regarded as an apex.